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(71) 出願人 590000846
イーストマン コダック カンパニー
アメリカ合衆国, ニューヨーク14650, ロ
チェスター, ステイト ストリート343

(72) 発明者 デイビッド アートマン
アメリカ合衆国, ニューヨーク 14618,
ロチェスター, ウェストランド アベニュー
119

(74) 代理人 100077517
弁理士 石田 敬 (外4名)

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(54) 【発明の名称】 インクジェット印刷方法

(57) 【要約】

【課題】 改良された耐オゾン堅牢度および物理的耐久性 (例えば耐掻き傷性および耐汚れ性) を有する画像を提供する。

【解決手段】 A) デジタルデータ信号に応答するインクジェットプリンターを用意する工程、B) 上記プリンターに、連続ボイドを有する連続的で同一の広がりをもつ多孔質のインク受容層を担持している支持体を有するインク受容要素を装填する工程、C) 上記プリンターに、水、湿潤剤、顔料、および水分散性ポリマーの粒子のインクジェットインク組成物を装填する工程、並びにD) 上記デジタルデータ信号に応答して上記インクジェットインクを使用して上記インク受容層上に印刷する工程、を有するインクジェット印刷方法。

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【特許請求の範囲】

【請求項 1】 A) デジタルデータ信号に応答するインクジェットプリンターを用意する工程、

B) 前記プリンターに、連続ボイドを有する連続的で同一の広がりをもつ多孔質のインク受容層を担持している支持体を含んでなるインク受容要素を装填する工程、

C) 前記プリンターに、水、湿潤剤、顔料、および水分分散性ポリマーの粒子を含んでなるインクジェットインク組成物を装填する工程、並びに

D) 前記デジタルデータ信号に応答して前記インクジェットインクを使用して前記インク受容層上に印刷する工程、を含むインクジェット印刷方法。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、水分分散性ポリマーを含有しているインク組成物を用いるインクジェット印刷方法に関する。

【0002】

【従来の技術】インクジェット印刷は、デジタル信号に20 応答して基材（紙、透明フィルム、布帛など）にインク液滴を付着させることによって画像を生じさせる非衝撃式の方法である。インクジェットプリンターには、産業上のラベル貼付から卓上文書および絵画像形成のための短時間印刷までの範囲にわたる市場の端々までの広範な用途がある。

【0003】インクジェット記録方法においては、使用されているインクが、種々の性能要求条件を満たすことが必要である。これらの性能要求条件は、一般に、筆記具（例えば、万年筆、フェルトペンなど）のためなどの他の液体インク用途よりも厳しい。特に、インクジェッ30 ト印刷方法において利用されるインクには、一般に、以下の条件が必要とされる。

【0004】（1）インクは、印刷装置の放電条件（例えば圧電発振器の駆動電圧および駆動周波数）、プリントヘッドのオリフィスの形および材料、オリフィスの直径などに合う粘度、表面張力、および導電性などの物理的性質を有するべきである。

【0005】（2）インクは、使用時にプリントヘッドのオリフィスを詰まらせることなく長期間にわたって保管することが可能であるべきである。

【0006】（3）インクは、記録媒体（例えば紙、フィルムなど）の上に迅速に定着されて、得られるインクドットの輪郭が平滑になり、インクドットの吸い取りが最小になることができるべきである。

【0007】（4）印刷される画像は、高品質であり（例えばクリアな色調を有する）、高い光沢および広い色域を有するべきである。

【0008】（5）印刷される画像は、優秀な耐水堅牢度（耐水性）および耐光堅牢度（耐光性）を呈するべきである。

【0009】（6）印刷される（インク）画像は、画像受容要素の表面に対する良好な接着性を有するべきであり、耐久性があり、物理的および機械的な掻き傷または損傷に対する耐性が高いものであるべきである。

【0010】（7）インクは、周囲の材料（例えばインク保管容器、プリントヘッド構成部品、オフィスなど）に化学的に作用したり、腐食したり、または浸食したりするべきではない。

【0011】（8）インクは、不快な臭いを有するべきではなく、毒性または可燃性であるべきではない。

【0012】（9）インクは、低い発泡特性および高い pH 安定特性を呈するべきである。

【0013】種々のインクジェットプリンターにおいて使用されるインクは、染料系または顔料系のいずれかに分類することができる。染料は、分散媒によって分子的に分散または溶媒和される着色剤である。分散媒は、室温において液体であっても固体であってもよい。一般的に使用される分散媒は、水または水と有機補助溶媒との混合物である。各々の個々の染料分子は、分散媒の分子によって取り囲まれている。染料系インクにおいては、顕微鏡下で粒子をまったく観察することができない。最近、染料系インクジェットインクの技術において多くの進歩があったけれども、これらのインクは、普通紙上での低い光学濃度および耐光堅牢性不良などの欠点を未だに有する。分散媒として水を使用する場合、このようなインクは、一般に、耐水堅牢性不良という欠点をも有する。

【0014】顔料系インクは、これらの制限に取り組むための手段として人気を博しつつある。顔料系インクにおいては、着色剤は、別個の粒子として存在する。これらの粒子は、通常は、顔料粒子の凝集および／または沈降を抑制するのに役立つ分散剤または安定剤として知られる添加剤で処理される。

【0015】顔料系インクは、染料系インクとは異なる欠点を有する。1つの欠点は、顔料系インクが、特別なコート紙およびコーテッドフィルム（例えば頭上投影に使用される透明フィルム並びに高品質グラフィックスおよびピクトリアル出力に使用される光沢紙および不透明な白色フィルム）と異なる相互作用をするということである。特に、コート紙およびコーテッドフィルムの表面全体にわたる画像領域を顔料系インクで作ると、乾燥接着性および湿潤接着性が不良であり、容易に汚れ得る画像になることが認められた。近年、高い光沢と、速乾能力を提供するための高い多孔率とを兼備するインクジェット受容体が開発された。しかしながら、高光沢受容体上では、引き掻き傷汚れがより目立つ。インクジェット受容要素の表面に、改良された耐久性および耐汚れ性を有する画像を印刷するのに使用することができる顔料系インク組成物を提供する必要がある。

【0016】オゾンは、一般に、海水面における空気中

に、10～50 PPBの濃度で存在する。オゾン濃度は、特定の条件下でのみ、これらのレベルを超える。しかしながら、低いオゾン濃度においてさえ、インクジェット染料およびインクジェット顔料などの染料および顔料は、通気性が高い場合（例えば多孔質光沢受容体に印刷される場合）に、非常に感受性が高く、大幅に退色する。

【0017】屋外用途用に設計されたインクジェット受容体は、顔料系インクで印刷されると、良好な耐久性を有する傾向があるけれども、それらもまた、高い通気性によってオゾンに暴露されると、大幅に退色する。

【0018】米国特許第 5,716,436号明細書および特開 2000-290553号公報において、普通紙に印刷されるインクジェットインクにおいて水分散性ポリマーを使用することが開示されている。しかしながら、これらのインクを用いて印刷される画像は、光学濃度が低く、耐湿潤摩耗性が非常に不十分であり、屋外用途には耐えないであろう。

【0019】英国特許第 2 351 292号は、反応生成物を含んでなる水散逸性ポリマーを含有しているインクジェットインク組成物に関する。しかしながら、この特許には、これらの組成物を普通紙以外の受容体上に使用することは開示されていない。

【0020】

【発明が解決しようとする課題】本発明の目的は、水分散性ポリマーを含有しているインクジェットインク組成物を使用するインクジェット印刷方法を提供することであり、このインク組成物を使用してインクジェット受容要素の表面に印刷される画像は、改良された耐オゾン堅牢度および物理的耐久性（例えば耐掻き傷性および耐汚れ性）を有する。

【0021】

【課題を解決するための手段】この目的および他の目的は、

- A) デジタルデータ信号に応答するインクジェットプリンターを用意する工程、
- B) 上記プリンターに、連続ボイドを有する連続的で同一の広がりをもつ多孔質のインク受容層を担持している支持体を含んでなるインク受容要素を装填する工程、
- C) 前記プリンターに、水、湿潤剤、顔料、および水分散性ポリマーの粒子を含んでなるインクジェットインク組成物を装填する工程、並びに
- D) 前記デジタルデータ信号に応答して前記インクジェットインクを使用して前記インク受容層上に印刷する工程、を含むインクジェット印刷方法、に関する本発明によって達成される。

【0022】多孔質受容体と水分散性ポリマーの粒子を含有しているインク組成物とを使用する本発明のインクジェット印刷方法により、改良された耐オゾン堅牢度および物理的耐久性（例えば耐掻き傷性および耐汚れ性）を有する画像が提供される。

【0023】

【発明の実施の形態】本発明において用いられるインク受容要素のための支持体は、紙、樹脂コート紙、プラスチック（例えばポリオレフィンタイプの樹脂もしくはポリエステルタイプの樹脂（例えばポリエチレンテレフタレート）、ポリカーボネート樹脂、ポリスルホン樹脂、メタクリル樹脂、セロハン、アセテートプラスチック、二酢酸セルロース、三酢酸セルロース、塩化ビニル樹脂、ポリエチレンナフタレート、ポリエステルジアセテート）、種々のガラス材料など、または開放気孔構造を含むもの（例えばポリオレフィンもしくはポリエステルから作られるもの）であってもよい。本発明において用いられる支持体の厚みは、例えば、12～500 μm 、好ましくは75～300 μm とすることができる。

【0024】本発明の好ましい態様において、上記連続的で同一の広がりをもつ多孔質のインク受容層は、有機粒子または無機粒子を含有している。使用してもよい有機粒子の例には、コア/シェル粒子（例えば2000年6月30日に出願された Kapusniakの米国特許出願第09/609/969号明細書において開示されているもの）、および均質粒子（例えば欧州特許出願第 0120331.3号明細書において開示されているもの）が含まれる。

【0025】使用してもよい有機粒子の例には、アクリル樹脂、スチレン樹脂、セルロース誘導体、ポリビニル樹脂、エチレン-アリルコポリマー、および重縮合ポリマー（例えばポリエステル）が含まれる。

【0026】本発明において使用してもよい無機粒子の例には、シリカ、アルミナ、二酸化チタン、クレー、炭酸カルシウム、硫酸バリウム、または酸化亜鉛が含まれる。

【0027】本発明の好ましい態様において、上記多孔質インク受容層は、20%～100%の粒子および0%～80%の高分子バインダー、好ましくは80%～95%の粒子および20%～5%の高分子バインダーを含んでなる。上記高分子バインダーは、親水性ポリマー（例えばポリビニルアルコール、ポリビニルピロリドン、ゼラチン、セルロースエーテル、ポリオキサゾリン、ポリビニルアセトアミド、部分的に加水分解されたポリ（酢酸ビニル-co-ビニルアルコール）、ポリアクリル酸、ポリアクリルアミド、ポリアルキレンオキシド、スルホン化もしくはリン酸化されたポリエステルおよびポリスチレン、カゼイン、ゼイン、アルブミン、キチン、キトサン、デキストラン、ペクチン、コラーゲン誘導体、コロジアン(colloidian)、寒天、クズウコン、ガー、カラギナン、トラガカント、キサントラン、ラムサン(rhamsan) など）であってもよい。好ましくは、上記親水性ポリマーは、ポリビニルアルコール、ヒドロキシプロピルセルロース、ヒドロキシプロピルメチルセルロース、ポリアルキレンオキシド、ポリビニルピロリドン、ポリ酢酸ビニル、もしくはこれらのコポリマー、またはゼラチンである。

【0028】インクジェット記録要素に機械的耐久性を付与するために、上記で考察したバインダーに作用する架橋剤を少量添加してもよい。このような添加剤は、層の結合力を改良する。例えばカルボジイミド、多官能価アジリジン、アルデヒド、イソシアネート、エポキシド、多価金属カチオン、ビニルスルホン、ピリジニウム、ピリジリウム(pyridylum)ジカチオンエーテル、メトキシアルキルメラミン、トリアジン、ジオキサン誘導体、クロム明礬、硫酸ジルコニウムなどの架橋剤を使用することができる。好ましくは、架橋剤は、アルデヒド、アセタール、またはケタール（例えば2,3-ジヒドロキシ-1,4-ジオキサン）である。

【0029】本明細書において使用されているように、多孔質インクジェット受容層は、通常は、バインダーによっていっしょに結合された無機粒子または有機粒子を含んでなる。このタイプのコーティングにおける粒子の量は、臨界粒子体積濃度をはるかに超えていることが多く、その結果、コーティングの多孔率が高くなる。インクジェット印刷方法において、インク液滴は、毛管作用によってコーティング中に迅速に吸収され、画像は、プリンターから出てきた直後に指触乾燥状態にある。ゆえに、多孔質コーティングにより、インクの速い「乾燥」が可能となり、耐汚れ性を有する画像が生ずる。

【0030】また、上記多孔質インク受容層は、開放気孔ポリオレフィン、開放気孔ポリエステル、または開放気孔膜を含むこともできる。開放気孔膜は、相の反転という既知の技法によって形成させることができる。開放気孔膜を含んでなる多孔質インク受容層の例は、欧州特許出願第01202701.7号および同01202711.6号の各明細書において開示されている。

【0031】本発明において用いてもよい顔料には、単独または組み合わされた、有機顔料および無機顔料（例えば、米国特許第5,026,427号、同5,086,698号、同5,141,556号、同5,160,370号、および同5,169,436号の各明細書において開示されているもの）が含まれる。顔料の厳密な選択は、特定の用途および性能要求条件（例えば色再現および画像安定性）に依存するであろう。本発明における使用に好適な顔料には、例えば、アゾ顔料、モノアゾ顔料、ジスアゾ顔料、アゾ顔料レーキ、 β -ナフトール顔料、ナフトールAS顔料、ベンゾイミダゾロン顔料およびイソインドリン(isoindoline)顔料、多環式顔料、フタロシアニン顔料、キナクリドン顔料、ペリレン顔料およびペリノン顔料、チオインジゴ顔料、アントラピリミドン顔料、フラバントロン顔料、アントアントロン(anthanthrone)顔料、ジオキサジン顔料、トリアリールカルボニウム顔料、キノフタロン顔料、ジケトピロロピロール顔料、二酸化チタン、酸化鉄、並びにカーボンブラックが含まれる。

【0032】使用してもよい顔料の典型例には、カラーインデックス(C. I.)ピグメントイエロー1、2、

3、5、6、10、12、13、14、16、17、62、65、73、74、75、81、83、87、90、93、94、95、97、98、99、100、101、104、106、108、109、110、111、113、114、116、117、120、121、123、124、126、127、128、129、130、133、136、138、139、147、148、150、151、152、153、154、155、165、166、167、168、169、170、171、172、173、174、175、176、177、179、180、181、182、183、184、185、187、188、190、191、192、193、194; C. I. ピグメントオレンジ1、2、5、6、13、15、16、17:1、19、22、24、31、34、36、38、40、43、44、46、48、49、51、59、60、61、62、64、65、66、67、68、69; C. I. ピグメントレッド1、2、3、4、5、6、7、8、9、10、11、12、13、14、15、16、17、18、21、22、23、31、32、38、48:1、48:2、48:3、48:4、49:1、49:2、49:3、50:1、51、52:1、52:2、53:1、57:1、60:1、63:1、66、67、68、81、95、112、114、119、122、136、144、146、147、148、149、150、151、164、166、168、169、170、171、172、175、176、177、178、179、181、184、185、187、188、190、192、194、200、202、204、206、207、210、211、212、213、214、216、220、222、237、238、239、240、242、243、245、247、248、251、252、253、254、255、256、258、261、264; C. I. ピグメントバイオレット1、2、3、5:1、13、19、23、25、27、29、31、32、37、39、42、44、50; C. I. ピグメントブルー1、2、9、10、14、15:1、15:2、15:3、15:4、15:6、15、16、18、19、24:1、25、56、60、61、62、63、64、66; C. I. ピグメントグリーン1、2、4、7、8、10、36、45; C. I. ピグメントブラック1、7、20、31、32、およびC. I. ピグメントブラウン1、5、22、23、25、38、41、42が含まれる。

【0033】本発明の好ましい態様において、用いられる顔料は、C. I. ピグメントブルー15:3、C. I. ピグメントレッド122、C. I. ピグメントイエロー155、C. I. ピグメントイエロー74、ビス(フタロシアニルアルミノ)テトラフェニルジシロキサ

ンまたはC. 1. ピグメントブラック7である。

【0034】本発明において用いられるインク組成物のための水性分散媒は、水または水と少なくとも1種の水混和性補助溶媒との混合物である。好適な混合物の選択は、特定の用途（例えば所望の表面張力および粘度、選ばれる顔料、顔料が加えられたインクジェットインクの乾燥時間、並びにインクが印刷される紙のタイプ）に依存する。選ぶことができる水混和性補助溶媒の代表例には、（1）アルコール（例えばメチルアルコール、エチルアルコール、n-プロピルアルコール、イソプロピルアルコール、n-ブチルアルコール、s-ブチルアルコール、t-ブチルアルコール、イソブチルアルコール、フルフリルアルコール、およびテトラヒドロフルフリルアルコール）、（2）ケトンまたはケトアルコール（例えばアセトン、メチルエチルケトン、およびジアセトンアルコール）、（3）エーテル（例えばテトラヒドロフランおよびジオキサン）、（4）エステル（例えば、酢酸エチル、乳酸エチル、炭酸エチレン、および炭酸プロピレン）、（5）多価アルコール（例えばエチレングリコール、ジエチレングリコール、トリエチレングリコール、テトラエチレングリコール、プロピレングリコール、ポリエチレングリコール、グリセロール、2-メチル-2,4-ペンタンジオール、1,2,6-ヘキサントリオール、およびチオグリコール）、（6）アルキレングリコールから誘導される低級アルキルモノエーテルおよび低級アルキルジエーテル（例えばエチレングリコールモノメチル（またはエチル）エーテル、ジエチレングリコールモノメチル（またはエチル）エーテル、ジエチレングリコールモノブチル（またはエチル）エーテル、プロピレングリコールモノメチル（またはエチル）エーテル、ポリエチレングリコールブチルエーテル、トリエチレングリコールモノメチル（またはエチル）エーテル、およびジエチレングリコールジメチル（またはエチル）エーテル）、（7）窒素含有環式化合物（例えばピロリドン、N-メチル-2-ピロリドン、および1,3-ジメチル-2-イミダゾリジノン）、並びに（8）硫黄含有化合物（例えばジメチルスルホキシド、2,2'-チオジエタノール、およびテトラメチレンスルホン）が含まれる。

【0035】一般に、顔料系インクジェットインクを濃厚ミル粉砕物の形で作るのが望ましく、これは、後に、インクジェット印刷システムにおいて使用するのに適切な濃度に希釈される。この技法により、より大量の顔料系インクを装置から調製することが可能となる。上記ミル粉砕物が溶媒中で作られた場合は、それを水および任意選択的に他の溶媒で希釈して、適切な濃度とする。上記ミル粉砕物が水中で作られた場合は、それをさらなる水または水混和性溶媒で希釈して、所望の濃度とする。希釈によって、インクが、個々の用途に望ましい粘度、色、色相、飽和濃度、および印刷領域付着量に調整される。ミル粉砕物の調製方法については、米国特許第 5,6

79,138号、同 5,670,139号、および同 6,152,999号の各明細書において開示されている。本発明の好ましい態様においては、分散剤もまた、インクジェットインク組成物に添加され、粉砕過程において顔料をサブミクロンの大きさに破壊するのに使用され、コロイド状分散体を、長期間にわたって、安定に保ち、凝集が無いようにする。

【0036】有機顔料の場合には、インクはおおよそ30質量%に及ぶ顔料を含有することができるけれども、一般には、殆どのインクジェット印刷用途において、全インク組成物のおおよそ 0.1~10質量%、好ましくは 0.1~5質量%の範囲にあるであろう。無機顔料が選ばれる場合、一般に、無機顔料は有機顔料よりも高い比重を有するので、インクは、有機顔料を用いる同等のインクよりも、より高い質量%の顔料を含有する傾向があり、場合によっては、おおよそ75%もの高い含有量となる場合がある。

【0037】用いられる水性分散媒の量は、インク的全質量に対して、おおよそ70~99質量%、好ましくはおおよそ90~98質量%の範囲にある。水と多価アルコール（例えばジエチレングリコール）との混合物は、水性分散媒として有用である。好ましい態様において、インクは、5~60質量%の水混和性溶媒を含有している。百分率は水性分散媒の全質量に対するものである。

【0038】本発明において用いられる水分散性ポリマーの粒子は、一般に、1 μm 未満、好ましくは 0.5 μm 未満、より好ましくは 0.25 μm 未満の平均粒径を有する。

【0039】本発明において使用される水分散性ポリマーは、一般に、水性媒体中で安定化され得るいずれの組成の疎水性ポリマーであってもよい。このような疎水性ポリマーは、一般に、縮合ポリマーまたは付加ポリマーのいずれかに分類される。縮合ポリマーには、例えば、ポリエステル、ポリアミド、ポリウレタン、ポリウレア、ポリエーテル、ポリカーボネート、多酸無水物、および上述のタイプの組み合わせを含んでなるポリマーが含まれる。付加ポリマーは、例えば、アリル化合物、ビニルエーテル、ビニル複素環式化合物、スチレン、オレフィン、およびハロゲン化オレフィン、エチレン系不飽和カルボン酸およびそれらから誘導されるエステル、不飽和ニトリル、ビニルアルコール、アクリルアミドおよびメタクリルアミド、ビニルケトン、多官能価モノマーなどのビニルタイプのモノマーの重合によって形成されるポリマー、またはこれらのモノマーの種々の組み合わせから形成されるコポリマーである。

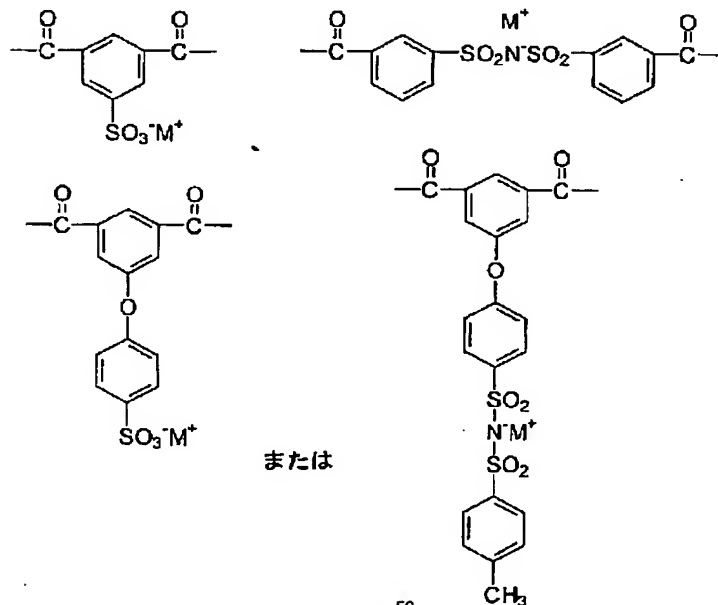
【0040】好ましい水分散性ポリマーの第1の種類には、水性エマルション中でのビニルモノマーのラジカル重合によって調製されるスチレン/アクリル系ポリマーが含まれる。このスチレン/アクリル系ポリマーに好適なモノマーは、例えば、米国特許第 5,594,047号明細書

において開示されているように、当該技術分野においてよく知られている。本発明の好ましい態様において、このスチレン/アクリル系ポリマーのためのモノマーは、アクリル酸のエステル、メタクリル酸のエステル、スチレン、またはスチレン誘導体である。

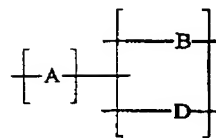
【0041】例えば、上記スチレン/アクリル系ポリマーのためのモノマーは、メタクリル酸メチル、メタクリル酸エチル、メタクリル酸ブチル、アクリル酸エチル、アクリル酸ブチル、アクリル酸ヘキシル、アクリル酸n-オクチル、メタクリル酸ラウリル、メタクリル酸2-エチルヘキシル、アクリル酸ノニル、メタクリル酸ベンジル、メタクリル酸2-ヒドロキシプロピル、アクリロニトリル、メタクリロニトリル、酢酸ビニル、プロピオン酸ビニル、塩化ビニリデン、塩化ビニル、スチレン、t-ブチルスチレン、ビニルトルエン、ブタジエン、イソプレン、N,N-ジメチルアクリルアミド、アクリル酸、メタクリル酸、クロロメタクリル酸、マレイン酸、アリルアミン、N,N-ジエチルアリルアミン、ビニルスルホンアミド、アクリル酸ナトリウム、メタクリル酸ナトリウム、アクリル酸アンモニウム、メタクリル酸アンモニウム、アクリルアミドプロパン-塩化トリエチルアンモニウム、メタクリルアミドプロパン-塩化トリエチルアンモニウム、塩酸ビニルピリジン、ビニルホスホン酸ナトリウム、および1-メチルビニルホスホン酸ナトリウム、ビニルスルホン酸ナトリウム、1-メチルビニルスルホン酸ナトリウム、2-アクリルアミド-2-メチル-1-プロパンスルホン酸ナトリウム、またはスチレンスルホン酸ナトリウムから形成させることができる。

【0042】本発明において使用してもよい水分散性ポリマーの第2の種類には、水性分散性ポリエステルアイオノマーが含まれる。好ましい態様において、これらのポリエステルアイオノマーは、以下の構造を有する。

【0043】



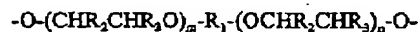
【化1】



【0044】上式中、Aは、100モル%の反復単位をいっしょになって含んでなる1種以上のジオール成分の残基であって、以下の構造によって表される。

【0045】

【化2】



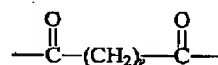
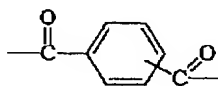
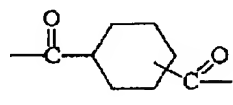
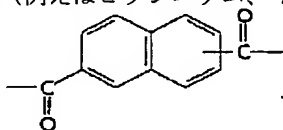
【0046】上式中、mおよびnは、独立に、0～4の整数を表し、R₁は、S、1～16個の炭素原子を有するアルキレン基、5～20個の炭素原子を有するシクロアルキレン基、8～20個の炭素原子を有するシクロビスアルキレン基、7～16個の炭素原子を有するビスシクロアルキレン基もしくはトリシクロアルキレン基、9～18個の炭素原子を有するビスシクロビスアルキレン基もしくはトリシクロビスアルキレン基、8～20個の炭素原子を有するアリーレン基、カルビトール末端基を有するポリジメチルシロキサンセグメントを表し、そしてR₂およびR₃は、各々独立に、H、1～6個の炭素原子を有する置換もしくは未置換のアルキル基または6～12個の炭素原子を有する置換もしくは未置換のアリール基を表す。

【0047】Bは、8～50モル%の反復単位を含んでなる二酸成分の残基であって、以下の構造の1種以上によって表される。

【0048】

【化3】

【0049】上式中、 M^+ は、アルカリ金属（例えばLi、Na、およびK）、アンモニウム基（例えばアンモニウム、メチルアンモニウム、トリエチルアンモニウム、テトラアルキルアンモニウム、アリールトリアルキルアンモニウムなど）、ホスホニウム基（例えばトリフェニルホスホニウム、テトラブチルホスホニウム）、複素芳香族アンモニウム基（例えばピリジニウム、イミダ



または

【0052】上式中、 p は、2～12の整数を表す。

【0053】上記式におけるAが表す典型的なジオールの中には、エチレングリコール、ジエチレングリコール、トリエチレングリコール、チオジエタノール、シクロヘキサジメタノール、ビスフェノールA、トランス-1,4-シクロヘキサジオール、ドデカンジオール、シス-エキソ-2,3-ノルボルナジオール、5-ノルボルネン-2,2-ジメタノール、ヒドロキノンビス(2-ヒドロキシエチルエーテル)、カルビトール末端基を有するポリジメチルシロキサン (MW=1000(DMS-C15)、(Gelest Inc.)) などが含まれる。

【0054】本発明において有用な水分散性ポリエステル具体例には、Eastman AQ (商標) ポリエステル (Eastman Chemical Company) が含まれる。Eastman のポリエステル、AQ 29 (商標)、AQ 38 (商標)、および AQ 55 (商標) は、異なる量のイソフタル酸、スルホイソフタル酸ナトリウム、ジエチレングリコール、および1,4-シクロヘキサジメタノールを含んでなる。これらの熱可塑性非晶質イオン性ポリエステルは、高温および低圧における熔融相縮重合によって調製され、この熔融生成物は小さなペレットに押出される。この固体ポリマーは最小限の撹拌により70℃の水に容易に分散し、さらなる界面活性剤または溶媒をまったく含有していない半透明の低粘度分散体を生ずる。イオン性モノマー（すなわち、スルホイソフタル酸）の量を変えることにより、粒径を制御することができる。粒径は0.02～0.1μmの範囲にわたる。

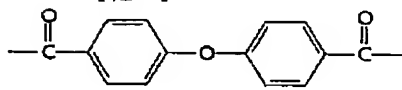
【0055】本発明において使用してもよい水分散性ポリマーの第3の種類には、水性分散性ポリウレタンが含まれる。有用なポリウレタンの例は、欧州特許出願第01201186.2号明細書において開示されている。これらの材料は、"Polyurethane Handbook", Hanser Publishers, Munich Vienna, 1985 に記載されているように調製する

ポリウム、およびN-メチルアンモニウム)、スルホニウム基、グアニジウム基、アミジニウム基などを表す。

【0050】Dは、50～92モル%の反復単位を含んでなる二酸成分の残基であって、以下の構造の1種以上によって表される。

【0051】

【化4】



ことができる。水性分散性ポリウレタンの例は、Witco Corp. による Witcobond (商標) ポリウレタン分散体およびBF Goodrich Company による Sancure (商標) ポリウレタンである。

【0056】本発明において使用してもよい水分散性ポリマーの第4の種類には、ポリウレタン-アクリル系ポリマーアロイが含まれる。有用なポリウレタン-アクリル系ポリマーアロイ分散体の例は、米国特許第 5,173,526号明細書において開示されている。このタイプの材料の例は、CK Witco Corporationによる Witcobond A-100であり、これは、ウレタンおよびポリアクリレートをベースとする脂肪族ポリエステルアロイである。

【0057】本発明において使用される水分散性ポリマーは、インクジェットインク中に、一般に 0.1～10質量%、好ましくは 0.5～5質量%存在する。

【0058】一般に、水分散性ポリマー粒子をインクに添加することにより、これらのインクが印刷された後の印刷領域において、受容体の表面の光沢レベルを高めることができることが認められた。

【0059】ジェット速度、液滴の分離長、液滴の大きさ、および流れの安定性は、一般に、インクの表面張力および粘度によって影響される。インクジェット印刷システムと共に使用するのに好適な顔料系インクジェットインクは、 $20 \times 10^{-5} \sim 60 \times 10^{-5}$ N/cm (20～60dyn/cm) の範囲、より好ましくは $30 \times 10^{-5} \sim 50 \times 10^{-5}$ N/cm (30～50dyn/cm) の範囲にある表面張力を有するべきである。水性インクにおける表面張力の制御は、少量の界面活性剤の添加によって達成される。使用されるべき界面活性剤の量は、単純な試行錯誤的な実験によって決定することができる。米国特許第 5,324,349号、同 4,156,616号、および同 5,279,654号の各明細書において開示されているもの並びにインクジェットインク技術分野において知られている他の界面活性剤の中から、アニオン性界面活

性剤およびカチオン性界面活性剤を選ぶことができる。市販の界面活性剤には、Air Products製のSurfynol（商標）、DuPont製の Zonyl（商標）、および3M製の Fluorad（商標）が含まれる。

【0060】インクが乾固したり、インクジェットプリントヘッドのオリフィス中で固まったりするのを防ぐのを助けるには、本発明の方法において用いられる組成物に湿潤剤を用いる。この目的のために本発明において用いられる組成物において有用な多価アルコール湿潤剤には、例えば、エチレングリコール、ジエチレングリコール、トリエチレングリコール、プロピレングリコール、テトラエチレングリコール、ポリエチレングリコール、グリセロール、2-メチル-2,4-ペンタンジオール、1,2,6-ヘキサントリオール、およびチオグリコールが含まれる。湿潤剤は、10～50質量%の濃度で用いることができる。好ましい態様において、ジエチレングリコールまたはグリセロールとジエチレングリコールとの混合物が、10～20質量%の濃度で用いられる。

【0061】上記インクは、広範な射出条件（すなわち、サーマルインクジェット印刷装置における駆動電圧およびパルス幅、ドロップーオンーデマンド式装置または連続式装置のいずれかにおける圧電素子の駆動周波数、並びにノズルの形状および大きさ）に適合する物理的性質を有する。

【0062】また、受容基材が高度にサイジング処理を施された紙である場合にはとりわけ、本発明の方法において用いられるインク組成物に浸透剤（0～10質量%）を添加して、インクが受容基材に浸透するのを助けてもよい。本発明において用いられるインクに好ましい浸透剤は、最終的な濃度が1～6質量%のn-プロパノールで

【0063】また、本発明の方法において用いられるインク組成物に殺生剤（0.01～1.0質量%）を添加して、経時によってインク中に発生することがある好ましくな

マゼンタ顔料分散体（MD-1）

ミル粉砕物

高分子ビーズ（平均直径=50 μm）

（粉砕媒体）

Sun Chemical Co.製のキナクリドンマゼンタ

（ピグメントレッド122）

オレイルメチルタウリン（OMT）カリウム塩

脱イオン水

Proxel GXL（商標）

（Zeneca製の殺生剤）

325 g

30 g

9 g

208 g

0.2 g

【0070】上記成分を、Morehouse-Cowles Hochmeyerによって製造された高エネルギー媒体ミルを使用して、BYK-Gardner から得られた2リットルの二重壁容器中で粉砕した。このミルは、室温においておよそ8時間運転した。VWR Scientific Products から得られた4～8 μmのKIMAX（商標）ブフナー漏斗によって上記ミル粉砕

い微生物の生育を防止してもよい。本発明において用いられるインクに好ましい殺生剤は、最終濃度が0.05～0.5質量%のProxel（商標）GXL（Zeneca Colours Co.）である。インクジェットインク中に任意選択的に存在していてもよいさらなる添加剤には、増粘剤、導電性増強剤、コゲーション防止剤、乾燥剤、および脱泡剤が含まれる。

【0064】本発明において用いられる水分散性ポリマーを使用して製造されるインクジェットインクは、インクジェットプリンターのプリントヘッドにおける複数のノズル（またはオリフィス）からインク液滴を射出することによって、液体インク液滴が制御された様式でインク受容基材に適用されるインクジェット印刷において用いられる。

【0065】市販のインクジェットプリンターは、多くの異なる方法を使用して、インク液滴の付着を制御している。このような方法としては、一般に、連続流式およびドロップーオンーデマンド式の2種類のタイプがある。

【0066】ドロップーオンーデマンド式システムにおいて、例えば、デジタルデータ信号に従って制御される圧電装置、音響装置、またはサーマル法によって生成される圧力によって、インクの液滴がオリフィスから直接にインク受容層の1つの位置に射出される。インク液滴は必要になるまでは生成されず、かつプリントヘッドのオリフィスから射出されない。インクジェット印刷方法（および関連するプリンター）は市販されており、詳細に説明する必要は無い。

【0067】以下の例は、本発明の有用性を説明するものである。

【0068】

【実施例】例1

以下の顔料分散体を調製した。

【0069】

物を濾過することによって、この分散体を粉砕媒体から分離した。

【0071】シアン顔料分散体（CD-1）

この分散体は、マゼンタ顔料の代わりにビス（フタロシアンルアルミノ）テトラフェニルジシロキサン（Eastman Kodak Co.）を使用し、18gのOMTを使用したこと

を除き、上記マゼンタ顔料分散体と同様に調製した。

【0072】イエロー顔料分散体 (YD-1)

この分散体は、マゼンタ顔料の代わりにピグメントイエロー 74 (Clariant Corporation) を使用し、3.75 g の OMT を使用したことを除き、上記マゼンタ顔料分散体と同様に調製した。

【0073】水分散性ポリマーの調製

ポリエステル分散体 1 (PE-1)

機械式攪拌機、有効還流凝縮器、および N₂ 注入口を備えた 500mL の三つ口丸底フラスコに、28.96 g の 5-スル
10 ホイソフタル酸ナトリウム、81.74 g のイソフタル酸、
45.37 g のジエチレングリコール、および 46.51 g のシ
クロヘキサジメタノールを装填した。このフラスコ
を、僅かな N₂ 気流下でゆっくりと攪拌しながら、220
℃の塩浴中に置いた。反応混合物が融解したときに、0.
51 g の Fascat 4100 (商標) 触媒を添加し、重合を 8.0
時間進行させたところ、理論量の水が留去された。この
コポリマーを、N₂ 雰囲気下で放冷し、次に、このポリ
マーをフラスコから取り出した。

【0074】機械式攪拌機および還流凝縮器を備えた 2
50mL の三つ口丸底フラスコに、80mL の脱イオン水を装填
し、85℃に加熱した。迅速に攪拌しながら、20.3 g の上
記ポリエステルアイオノマーを徐々に添加し、この分散
体を 85℃において 2 時間加熱した。加熱を止め、この分
散体を室温において終夜攪拌した。この混合物を濾過
し、18.7 質量% のポリマーを含有している僅かに曇った
分散体を 92.5 g 得た。

【0075】ポリエステル分散体 2 (PE-2)

機械式攪拌機、有効還流凝縮器、および N₂ 注入口を備
えた 500mL の三つ口丸底フラスコに、28.96 g の 5-スル
30 ホイソフタル酸ナトリウム、81.74 g のイソフタル酸、
41.72 g のジエチレングリコール、および 42.77 g のシ
クロヘキサジメタノールを装填した。このフラスコ
を、僅かな N₂ 気流下でゆっくりと攪拌しながら、220
℃の塩浴中に置いた。反応混合物が融解したときに、0.
49 g の Fascat 4100 (商標) 触媒を添加し、重合を 8.0
時間進行させたところ、理論量の水が留去された。この
コポリマーを、N₂ 雰囲気下で放冷し、次に、このポリ
マーをフラスコから取り出した。

【0076】機械式攪拌機および還流凝縮器を備えた 2
50mL の三つ口丸底フラスコに、80mL の脱イオン水を装填
し、85℃に加熱した。迅速に攪拌しながら、20.1 g の上
記ポリエステルアイオノマーを徐々に添加し、この分散
体を 85℃において 2 時間加熱した。加熱を止め、この分
散体を室温において 20 時間攪拌した。この混合物を濾過
し、19.1 質量% のポリマーを含有している僅かに曇った
分散体を 90.0 g 得た。

【0077】ポリエステル分散体 3 (PE-3)

固形 AQ-55 ポリエステルアイオノマーを Eastman Chemi
50 cal から購入し、次に、加熱および攪拌しながら水に添加

して、固形分 30% の濃度の AQ-55 分散体を得た。

【0078】ポリエステル分散体 4 (PE-4)

ポリエステル分散体 4 は、使用した出発原料を、164.29
g の 1,4-シクロヘキサジカルボン酸、46.30 g のスル
ホイソフタル酸ナトリウム、90.24 g のシクロヘキサ
ジメタノール、および 61.47 g の 1,10-デカンジオール
としたことを除き、ポリエステル分散体 2 と同じ手順に
従って調製した。

【0079】ポリウレタン分散体 1 (PU-1)

10 攪拌機、窒素注入口、および凝縮器を備えた 500mL のフ
ラスコに、148.12 g のスルホイソフタル酸ナトリウム、
530.00 g の Tone (商標) 0200 (Union Carbide から入手
可能なポリカプロラクトンポリオール、分子量 530)、
および 200 ppm のチタン (IV) イソプロポキシドを装填
した。攪拌しながら、この混合物を 250℃に加熱した。
この混合物が透明になったとき (およそ 2 時間) に、温
度を 270℃に上げ、さらに 2 時間維持した。およそ 15.8
g のメタノール凝縮液が収集されたときに、エステル交
換がほぼ完了したものとみなした。この反応生成物 (以
降、SIP-ジオールと呼ぶ) を瓶に入れ、さらに精製
すること無く使用した。

【0080】温度計、攪拌機、水凝縮器、および減圧排
気口を備えた 2 リットルの樹脂フラスコに、245.48 グラ
ム (0.19 モル) の SIP-ジオールを装填し、100℃に
おいて減圧下で脱水した。このフラスコを温度制御され
た浴の中に置いた。減圧を解き、40℃において、54.79
グラム (0.24 モル) のビスフェノール A、64.89 グラ
ム (0.72 モル) の 1,4-ブタンジオール、150 グラムの 2-
ブタノン、および 40 滴のジブチル錫ジラウレート (触
媒) を攪拌しながら反応フラスコに添加した。温度を 82
℃に上げて均質な溶液を得て、70℃に冷却し、続いて、
226.74 グラム (1.02 モル) のイソホロンジイソシアネート
および 10 グラムの 2-ブタノンを添加した。

【0081】温度を調整して 82℃に戻し、16 時間維持し
て、反応を完了させ、遊離イソシアネートを 3% 未満し
か含有していない最終的なポリウレタンを得た。遊離イ
ソシアネートの含有率は、波数 2240 のところの吸収ピー
クの赤外分光測定によって監視した。この反応フラスコ
に高剪断下で 2000 グラムの水を添加して、安定な水性分
散体を形成させた。減圧下で加熱することによって 2-ブ
タノンを除去して、固形分 40% の水性分散体を得た。

【0082】ポリウレタン分散体 2 (PU-2)

温度計、攪拌機、水凝縮器、および減圧排気口を備えた
2 リットルの樹脂フラスコに、123.0 g (0.041 モル)
の Tone (商標) 0260 (Union Carbide から入手可能なポ
リカプロラクトンポリオール、分子量 3000) を入れた。
これを、100℃において減圧下で脱水した。減圧を解
き、40℃において攪拌しながら以下のものを添加した。
22.70 g (0.166 モル) のジメチロールプロピオン酸、
50.90 g (0.241 モル) のビスフェノール A、63.58

g (0.706モル) の1,4-ブタンジオール、180 g の2-ブタノン、および20滴のジブチル錫ジラウレート (触媒)。温度を82℃に上げ、16時間維持して、反応を完了させ、遊離イソシアネートを3%未満しか含有していない中間体を得た。

【0083】遊離イソシアネートの含有率は、波数2240のところの吸収ピークの赤外分光測定によって監視した。この反応混合物を75 g のテトラヒドロフランで希釈し、45%の水酸化カリウム溶液19.7 g で中和して、ジメチロールプロピオン酸に対して理論的イオン化の95%を達成した。この中和された混合物に高剪断下で1300 g の蒸留水を添加して、安定な水性分散体を形成させ、続いて、減圧下で蒸発させて2-ブタノンを除去した。

【0084】ポリウレタン分散体3 (PU-3) ポリウレタン分散体3は、使用した出発原料を、51.6 g のKM101733 (Stahl Co.製ポリカーボネートポリオール、m.w. 860)、10.20 g のジメチロールプロピオン酸、10.0 g の2,2-オキシジエタノール、24.33 g の1,4-ブタンジオール、111.20 g のイソホロンジイソシアネートとしたことを除き、ポリウレタン分散体2と同様に調製した。

【0085】ポリアクリル系分散体1 (PA-1) 400 g の脱イオン水および0.6 g のOlin 10G (商標) 界面活性剤を、機械式攪拌機および窒素注入口を備えた1リットルの三つ口丸底フラスコに装填した。この溶液を、恒温浴中で、窒素で30分間パージし、80℃に加熱した。172.8 g のアクリル酸メチルおよび7.2 g の2-アクリルアミド-2-メチル-1-プロパンスルホン酸 (ナトリウム塩) を添加し、3分間攪拌した。16.4 g の10%過硫酸ナトリウム溶液および5.5 g の10%メタ重亜硫酸ナトリウム溶液を添加して、重合を開始させた。重合を1時間続け、80℃においてさらに1時間加熱した。温度を65~70℃に下げ、各々1 mL のt-ブチルブチルヒドロペルオキシド (10%) およびホルムアルデヒド-亜硫酸水素ナトリウム (10%) を後添加した。このラテックスを冷却し、濾過した。この分散体は、30質量%の固形分を含有していた。

表1

| ポリマー分散体 | 粒径 (nm) | 乾燥ポリマーのT _g (°C) | 重量平均分子量 |
|-------------|---------|----------------------------|------------|
| ポリエステル分散体1 | 308 | 23 | 3,400 |
| ポリエステル分散体2 | 295 | 38 | 4,125 |
| ポリエステル分散体3 | 19.9 | 55 | 18,000 |
| ポリエステル分散体4 | 110.2 | 6 | 10,400 |
| ポリウレタン分散体1 | 143.2 | 44 | 5,580 |
| ポリウレタン分散体2 | 18.0 | 80 | 17,400 |
| ポリウレタン分散体3 | 8.2 | 71 | 20,600 |
| ポリアクリル系分散体1 | 100 | 25 | >1,000,000 |
| ポリアクリル系分散体2 | 86 | 0 | >1,000,000 |

【0086】ポリアクリル系分散体2 (PA-2)

ポリアクリル系分散体2は、モノマー混合物を、14.17 g のメタクリルアミド、106.2 g のアクリル酸ブチル、14.17 g の2-アクリルアミド-2-メチル-1-プロパンスルホン酸 (ナトリウム塩)、および45.36 g のスチレンからなるものとし、使用した界面活性剤を、Olin 10Gの代わりにラウリル硫酸ナトリウムとしたことを除き、ポリアクリル系分散体1と同様に調製した。この分散体は、30質量%の固形分を含有していた。

【0087】ポリアクリル系分散体3 (PA-3)

ポリアクリル系分散体3は、25グラムのJonrez IJ-4655 (Westvaco Corporationから得られるスチレン-アクリル系ポリマー) を66グラムの水および9 g のトリエタノールアミンと、上記ポリマーが完全に溶解するまで混合することによって調製した。

【0088】ポリマー特性

ガラス転移温度

乾燥ポリマー材料のガラス転移温度 (T_g) は、20℃/分の加熱速度を使用して、示差走査熱分析 (DSC) によって測定した。T_g は、本明細書においては、ガラス転移の変曲点として定義される。

【0089】粒径測定

すべての粒子について、rookhaven Instruments Corporation によって製造された 90plus Particle Sizerによって特性決定を行った。容量平均直径を以下に列挙する。

【0090】平均分子量

上記試料について、3本のPolymer Laboratories plgl (商標) 小型混合 (mini-mixed) B カラムを使用するテトラヒドロフラン中でのサイズ排除クロマトグラフィー (SEC) によって分析した。このカラムの組は、580~2,300,000の、分子量分布が狭いポリスチレン標準を用いて校正した。

【0091】上記各種ポリマー特性を以下の表Iに要約する。

【0092】

【表1】

分を室温において穏やかに攪拌しながら混合することによって調製した。最終的な混合物のpHは、トリエタノールアミンの添加によって8.5に調整した。顔料および水分散性ポリマーの他に、10質量%のグリセロール、23質量%のトリエチレングリコール、および2.5質量%のDowanol DPM (商標) をもインクに含有させた。

【0094】本発明において用いられるインク並びに3種の比較用インクにおいて使用される顔料および水分散性ポリマーを、以下の表IIに示す。

【0095】

【表2】

表II

| インク | ポリマー分散体 | 顔料分散体 |
|------------|------------|------------|
| C-1 (対照標準) | 無し | CD-1 (2.5) |
| C-2 (対照標準) | 無し | MD-1 (2.9) |
| C-3 (対照標準) | 無し | YD-1 (2.9) |
| I-1 | PE-1 (2.5) | CD-1 (2.5) |
| I-2 | PE-2 (2.5) | CD-1 (2.5) |
| I-3 | PE-3 (2.5) | CD-1 (2.5) |
| I-4 | PA-1 (2.5) | CD-1 (2.5) |
| I-5 | PA-2 (2.5) | CD-1 (2.5) |
| I-6 | PU-3 (2.5) | CD-1 (2.5) |
| I-7 | PE-3 (2.5) | MD-1 (2.9) |
| I-8 | PE-4 (2.5) | MD-1 (2.9) |
| I-9 | PU-2 (2.0) | MD-1 (2.9) |
| I-10 | PA-3 (2.0) | MD-1 (2.9) |
| I-11 | PE-1 (2.5) | MD-1 (2.9) |
| I-12 | PU-1 (2.0) | MD-1 (2.9) |
| I-13 | PA-3 (2.0) | YD-1 (2.9) |

【0096】インクジェット記録要素

受容体1は、Xerox 4024DP普通紙 (対照標準) とした。

【0097】受容体2は、ポリエチレンコート紙上に2つの層を含んでなる多孔質光沢受容体とした。底部層は、ヒュームドアルミナ、Cab-O-Sperse PG003 (商標)

(Cabot Corp.)、ポリビニルアルコール、GH-23 (Nippon Gosei)、および2,3-ジヒドロキシ-1,4-ジオキサン (Clariant Corp.) を87:9:4の質量比で含んでなるものとし、厚みは38 μ mとした。頂部層は、Cab-O-Sperse PG003 (商標) (Cabot Corp.)、ポリビニルアルコール、GH-23 (Nippon Gosei)、界面活性剤 Zonyl FSN (商標) (DuPont Corp.)、および媒染材料MM

(以下の説明を参照されたい) を69:6:5:20の質量比で含んでなるものとし、厚みは2 μ mとした。

【0098】MMは、87質量%の塩化N-ビニルベンジル-N,N,N-トリメチルアンモニウムおよび13質量%のジビニルベンゼンから調製される、平均粒径が80nmの架橋ヒドロゲルポリマー粒子である。

【0099】受容体3は、Epson Photoglossy Paper

(商標) SP91001 (Epson Corporation) とした。これは、多孔質の光沢受容体である。

【0100】受容体4は、屋外用途のための EI Flame Retardant Banner (Eastman Kodak Company) とした。

【0101】受容体5は、屋外用途のための EI Water Resistant Self-Adhesive Vinyl (Eastman Kodak Company) とした。

【0102】受容体2~5は、いずれも、支持体上に連続的で同一の広がりをもつ多孔質のインク受容層を含んでなるインク受容要素である。

【0103】塗布された要素の調製

上述の受容体2に、16.3cm³/m² (16.3 cc/m²) でインクを塗布し、これらの要素を、試験の前に、20℃の室内条件において完全に乾燥させた。

【0104】耐湿潤摩耗性および耐乾燥摩耗性

上記インクを、上記インクジェット記録要素上に塗布した。インクが塗布された試料の表面に、直径がおおよそ2.54cmの水滴を2分間置き、その後、ペーパータオルを使用して過剰の水を優しく拭き取ることによって、耐湿潤摩耗性試験を行った。次に、上記の如く処理された領域を、直径3.5cmの領域上に200グラムの圧力で、乾いたペーパータオルで8回擦った。X-Rite (商標) 濃度計によって上記試験領域において測定されるステータスA反射濃度を記録し、試験前の光学濃度と比較した。耐湿潤摩耗性は、試験後に保持される光学濃度 (OD) の百分率として定義される。70%以上の耐湿潤摩耗性が望ましい。

【0105】耐乾燥摩耗性試験は、上記試料を、直径3.5cmの領域上に200グラムの圧力で、乾いたペーパータオルで8回擦ることによって行った。X-Rite (商標) 濃度計によって上記試験領域において測定されるステータスA反射濃度を記録し、試験前の光学濃度と比較した。耐乾燥摩耗性は、試験後に保持される光学濃度 (OD) の百分率として定義される。80%以上の耐湿潤摩耗性が望ましい。これらの結果を、以下の表IIIに列挙する。

【0106】耐オゾン性試験

各試料を、48~96時間にわたって、オゾンチャンバー (オゾン量5 ppm、相対湿度50%、21℃) 中で保管した。このオゾン暴露試験の前後で、X-Rite (商標) 414濃度計を使用して、ステータスA反射濃度を測定した。ステータスA濃度の保持率 (%) を計算した結果を、以下の表IIIに報告する。数値が大きいほど望ましく、オゾン暴露に対する画像の安定性がより良好であることを示す。

【0107】

【表3】

表III

| インク 番号 | インク 中の ポリマー | インク 中の 顔料 | 湿潤耐久性 (濃度保持率) (%) | 乾燥耐久性 (濃度保持率) (%) | 48時間 耐オゾン堅牢度 (濃度保持率) (%) |
|-----------|-------------------|-----------------|-------------------------|-------------------------|-----------------------------------|
| C-1 | 無し | CD-1 | 57 | 52 | 29 |
| I-1 | PE-1 | CD-1 | 69 | 110 | 108 |
| I-2 | PE-2 | CD-1 | 76 | 89 | 101 |
| I-3 | PE-3 | CD-1 | 67 | 98 | 102 |
| I-4 | PA-1 | CD-1 | 94 | 106 | 104 |
| I-5 | PA-2 | CD-1 | 51 | 87 | 98 |
| I-6 | PU-3 | CD-1 | 103 | 104 | 102 |
| C-2 | 無し | MD-1 | 30 | 63 | 94 |
| I-7 | PE-3 | MD-1 | 71 | 99 | 98 |
| I-8 | PE-4 | MD-1 | 99 | 102 | 98 |
| I-9 | PU-2 | MD-1 | 90 | 100 | 99 |
| I-10 | PA-3 | MD-1 | 62 | 92 | 98 |
| C-3 | 無し | YD-1 | 73 | 68 | 100 |
| I-13 | PA-3 | YD-1 | 93 | 95 | 102 |

【0108】上記結果は、本発明に係る多孔質光沢受容体2を使用している要素および水分散性ポリマーを含有しているインクにより、耐摩耗性および耐オゾン堅牢度が、比較用要素と比較して改良されたことを示している。

【0109】例2

以下に示す成分を有する一連のインクを、空のHewlett-

Packard HP 692C インクカートリッジに添加し、HP 692C プリンターに装填して、種々の受容体上に印刷した。これらの試料を、湿潤耐久性および耐オゾン堅牢度について試験した。結果を表IVに示す。

【0110】

【表4】

表IV

| インク 番号 | ポリマー | 顔料 | 受容体 | 印刷試料の 光学濃度 | 湿潤耐久性 (濃度保持率) (%) | 96時間 耐オゾン堅牢度 (濃度保持率) (%) |
|-----------|------|------|-------------|---------------|-------------------------|-----------------------------------|
| C-2 | 無し | MD-1 | 1 (対照標準) | 0.94 | 紙が崩壊した | 92 |
| I-11 | PE-1 | MD-1 | 1 (対照標準) | 0.69 | 紙が崩壊した | 94 |
| I-7 | PE-3 | MD-1 | 1 (対照標準) | 0.92 | 紙が崩壊した | 98 |
| I-12 | PU-1 | MD-1 | 1 (対照標準) | 0.90 | 紙が崩壊した | 94 |
| C-2 | 無し | MD-1 | 2 | 2.41 | 18 | 91 |
| I-11 | PE-1 | MD-1 | 2 | 2.36 | 74 | 98 |
| I-7 | PE-3 | MD-1 | 2 | 2.60 | 82 | 100 |
| I-12 | PU-1 | MD-1 | 2 | 1.89 | 53 | 99 |
| C-2 | 無し | MD-1 | 3 | 2.24 | 65 | 88 |
| I-11 | PE-1 | MD-1 | 3 | 2.04 | 72 | 97 |
| I-7 | PE-3 | MD-1 | 3 | 2.28 | 94 | 99 |
| I-12 | PU-1 | MD-1 | 3 | 1.82 | 96 | 96 |
| C-2 | 無し | MD-1 | 4 | 1.30 | 100 | 84 |
| I-11 | PE-1 | MD-1 | 4 | 1.28 | 100 | 86 |
| I-7 | PE-3 | MD-1 | 4 | 1.31 | 100 | 92 |
| I-12 | PU-1 | MD-1 | 4 | 1.30 | 100 | 86 |
| C-2 | 無し | MD-1 | 5 | 1.25 | 100 | 83 |
| I-11 | PE-1 | MD-1 | 5 | 1.18 | 100 | 84 |
| I-7 | PE-3 | MD-1 | 5 | 1.19 | 100 | 92 |
| I-12 | PU-1 | MD-1 | 5 | 1.24 | 100 | 88 |

【0111】上記結果は、普通紙(受容体1)上に印刷されたインクは、光学濃度が低く、耐久性が劣る画像を生じたのに対し、インクジェット受容体2～5上に印刷された場合には、より高い濃度およびより良好な耐久性

が認められたことを示している。さらに、水分散性ポリマーを含有している、本発明において用いられるインクを使用した場合には、耐オゾン堅牢度の改良が認められた。

【0112】例3

以下に示す成分を有する一連のインクを、空のHewlett-Packard HP 692C インクカートリッジに添加し、HP 692C プリンターに装填して、受容体2～5上にインクジェ

ット印刷した。これらの試料を、耐オゾン堅牢度について試験し、その結果を表Vに示す。

【0113】

【表5】

表V

| インク | ポリマー | 顔料 | 受容体 | 96時間 耐オゾン堅牢度 (濃度保持率) (%) |
|-----|------|------|-----|-----------------------------------|
| C-1 | 無し | CD-1 | 2 | 73 |
| I-1 | PE-1 | CD-1 | 2 | 99 |
| I-2 | PE-2 | CD-1 | 2 | 98 |
| I-3 | PE-3 | CD-1 | 2 | 98 |
| C-1 | 無し | CD-1 | 3 | 61 |
| I-1 | PE-1 | CD-1 | 3 | 99 |
| I-2 | PE-2 | CD-1 | 3 | 98 |
| I-3 | PE-3 | CD-1 | 3 | 98 |
| C-1 | 無し | CD-1 | 4 | 41 |
| I-1 | PE-1 | CD-1 | 4 | 93 |
| I-2 | PE-2 | CD-1 | 4 | 91 |
| I-3 | PE-3 | CD-1 | 4 | 94 |
| C-1 | 無し | CD-1 | 5 | 49 |
| I-1 | PE-1 | CD-1 | 5 | 69 |
| I-2 | PE-2 | CD-1 | 5 | 67 |
| I-3 | PE-3 | CD-1 | 5 | 80 |

【0114】上記結果は、水分散性ポリマーを含有している、本発明において用いられるインクが、大幅に改良された耐オゾン堅牢度を有することを示している。

【0115】本発明の他の好ましい態様を、請求項との関連において、次に記載する。

【0116】[1] A) デジタルデータ信号にตอบสนองするインクジェットプリンターを用意する工程、
B) 前記プリンターに、連続ボイドを有する連続的で同一の広がりをもつ多孔質のインク受容層を担持している支持体を含んでなるインク受容要素を装填する工程、
C) 前記プリンターに、水、湿潤剤、顔料、および水分散性ポリマーの粒子を含んでなるインクジェットインク組成物を装填する工程、並びに
D) 前記デジタルデータ信号にตอบสนองして前記インクジェットインクを使用して前記インク受容層上に印刷する工程、を含むインクジェット印刷方法。

【0117】[2] 前記水分散性ポリマーが、ポリエステル、ポリウレタン、またはポリアクリレートを含んでなる、[1]に記載の方法。

【0118】[3] 前記多孔質インク受容層が、20%～100%の粒子および0%～80%の高分子バインダーを含んでなる、[1]に記載の方法。

【0119】[4] 前記多孔質インク受容層が、50%～95%の粒子および50%～5%の高分子バインダーを含んでなる、[1]に記載の方法。

【0120】[5] 前記粒子が、シリカ、アルミナ、

二酸化チタン、クレー、炭酸カルシウム、硫酸バリウム、または酸化亜鉛を含んでなる、[3]に記載の方法。

【0121】[6] 前記高分子バインダーが、ポリビニルアルコール、ヒドロキシプロピルセルロース、ヒドロキシプロピルメチルセルロース、ポリアルキレンオキシド、ポリビニルピロリドン、ポリ酢酸ビニル、もしくはこれらのコポリマー、またはゼラチンである、[3]に記載の方法。

【0122】[7] 前記多孔質インク受容層が、有機粒子を含有している、[1]に記載の方法。

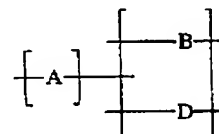
【0123】[8] 前記連続ボイドを有する連続的で同一の広がりをもつ多孔質のインク受容層が、高分子開放気孔膜を含んでなる、[1]に記載の方法。

【0124】[9] 前記水分散性ポリマーが、ポリエステルアイオノマーを含んでなる、[1]に記載の方法。

【0125】[10] 前記ポリエステルアイオノマーが、以下の一般式：

【0126】

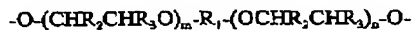
【化5】



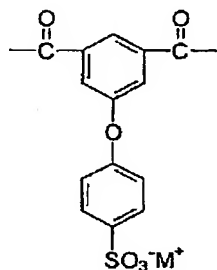
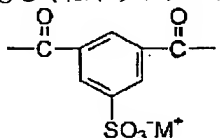
【0127】を有し、上式中、Aは、100モル%の反復単位をいっしょになって含んでなる1種以上のジオール成分の残基であって、以下の構造：

【0128】

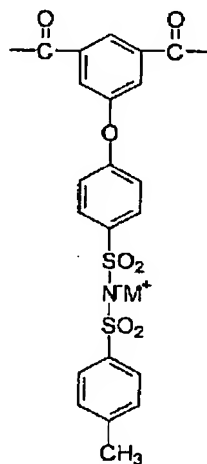
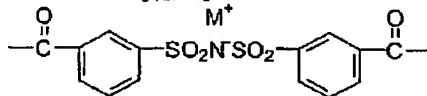
【化6】



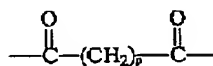
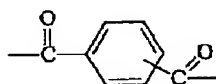
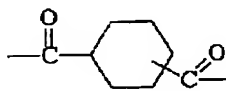
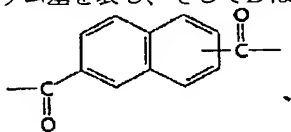
【0129】によって表され、上式中、mおよびnは、独立に、0～4の整数を表し、R₁は、S、1～16個の炭素原子を有するアルキレン基、5～20個の炭素原子を有するシクロアルキレン基、8～20個の炭素原子を有するシクロビスアルキレン基、7～16個の炭素原子を有するビスシクロアルキレン基もしくはトリシクロアルキレン



または



【0131】の1種以上によって表され、上式中、M⁺は、アルカリ金属、アンモニウム基、ホスホニウム基、複素芳香族アンモニウム基、スルホニウム基、グアニジウム基、またはアミジニウム基を表し、そしてDは、50



または

【0133】の1種以上によって表され、上式中、p

基、9～18個の炭素原子を有するビスシクロビスアルキレン基もしくはトリシクロビスアルキレン基、8～20個の炭素原子を有するアリービスアルキレン基もしくは6～12個の炭素原子を有するアリーレン基、カルビトール末端基を有するポリジメチルシロキサンセグメントを表し、そしてR₂ およびR₃ は、各々独立に、H、1～6個の炭素原子を有する置換もしくは未置換のアルキル基または6～12個の炭素原子を有する置換もしくは未置換のアリール基を表し、Bは、8～50モル%の反復単位を含んでなる二酸成分の残基であって、以下の構造：

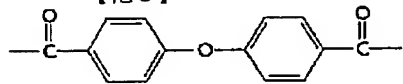
【0130】

【化7】

～92モル%の反復単位を含んでなる二酸成分の残基であって、以下の構造：

【0132】

【化8】



は、2～12の整数を表す、[9]に記載の方法。

フロントページの続き

- (72)発明者 ブルース クリニーン キャンベル
アメリカ合衆国, ニューヨーク 14626,
ロチェスター, メイロング ドライブ 14
- (72)発明者 エドガード ロベツ
アメリカ合衆国, ニューヨーク 14468,
ヒルトン, アップルウッド ウェイ 287
- (72)発明者 ホウエイリーン ヤウ
アメリカ合衆国, ニューヨーク 14625,
ロチェスター, ウェスト フィールド コ
モンズ 45

- (72)発明者 トーマス ウィリアム マーティン
アメリカ合衆国, ニューヨーク 14612,
ロチェスター, ウェスト ベンド ドライ
ブ 70
- (72)発明者 クリス ジー. ハン—アデベクン
アメリカ合衆国, ニューヨーク 14534—
4159, ピッツフォード, ワンダリング ト
レイル 25
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CLAIMS

[Claim(s)]

[Claim 1] A) The process which prepares the ink jet printer which answers a digital data signal, B) The process loaded with the ink acceptance element which comes to contain the base material which is supporting the ink absorbing layer of the porosity which has the continuous and same breadth which has a continuation void in said printer, C) The process which loads said printer with water, a wetting agent, a pigment, and the ink jet ink constituent that comes to contain the particle of a water-dispersion polymer, The ink jet printing approach including the process which answers the D aforementioned digital data signal at a list, and is printed on said ink absorbing layer using said ink jet ink.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the ink jet printing approach using the ink constituent containing a water-dispersion polymer.

[0002]

[Description of the Prior Art] Ink jet printing is the approach of the non-impact type which produces an image by answering a digital signal and making a liquid ink drop adhere to base materials (paper, a bright film, textile, etc.). There is an extensive application to some parts of the commercial scene covering the range from label pasting on industry to short-time printing for a desk document and pictures image formation in an ink jet printer.

[0003] In the ink jet record approach, it is required for the ink currently used to fulfill various engine-performance requirements. Generally these engine-performance requirements are severer than other liquid ink applications for writing implements (for example, a fountain pen, a felt pen, etc.) etc. Generally the following conditions are needed especially for the ink used in the ink jet printing approach.

[0004] (1) Ink should have physical properties, such as viscosity suitable for the diameter of the form of the discharge conditions (for example, driver voltage and drive frequency of a piezo oscillator) of an airline printer, and the orifice of a print head and an ingredient, and an orifice etc., surface tension, and conductivity.

[0005] (2) Ink can be kept over a long period of time, without blocking the orifice of a print head at the time of use.

[0006] (3) It is quickly fixed to ink on record media (for example, paper, a film, etc.), and the profile of the ink dot obtained becomes smooth, an ink dot inhales and picking becomes min.

[0007] (4) It should have gloss quality [the image printed] (for example, it has a clear color tone) and high and a large color gamut.

[0008] (5) The image printed should present excellent waterproof fastness (water resisting property) and color fastness to light (lightfastness).

[0009] (6) The image printed (ink) should have the good adhesive property over the front face of an image acceptance element, and should be durable, and its resistance over physical and mechanical a scratch or damage should be high.

[0010] (7) It should act on surrounding ingredients (for example, an ink storage container, a print head component part, an orifice, etc.) chemically, or should corrode, or ink should not be corroded.

[0011] (8) Ink should not be toxicity or inflammability rather than should have an unpleasant smell.

[0012] (9) Ink should present a low foaming property and high pH stability characteristics.

[0013] The ink used in various ink jet printers can be classified into either a color system or a pigment system. A color is distribution or a coloring agent by which a solvation is carried out in molecule by the dispersion medium. In a room temperature, a dispersion medium may be a liquid or may be a solid-state. The dispersion medium generally used is the mixture of water or water, and an organic auxiliary solvent. Each color molecule of each is surrounded with the molecule of a dispersion medium. In color system ink, a particle is unobservable at all under a microscope. Although there were many advances in the technique of color system ink jet ink recently, these ink usually has a

fault in the paper, low optical density and poor light fastness—proof still. When using water as a dispersion medium, generally such ink also has a fault of waterproof poor robustness.

[0014] Pigment system ink is winning popularity as a means for tackling these limits. In pigment system ink, a coloring agent exists as a separate particle. These particles are processed with the additive known as the dispersant which is usually useful to controlling condensation and/or sedimentation of a pigment particle, or a stabilizer.

[0015] Pigment system ink has a different fault from color system ink. I hear that pigment system ink carries out a different interaction from special coat paper and a special coated film (for example, the glossy paper and the opaque white film which are used for the bright film list used for overhead location projection by high quality graphics and the pictorial output), and one fault has it. When the image field covering coat paper and the whole front face of a coated film was especially made from pigment system ink, a desiccation adhesive property and a humid adhesive property are poor, and having become the image which may become dirty easily was admitted. In recent years, the ink jet acceptor which combines high gloss and the high porosity rate for offering quick-drying capacity was developed. However, on a high gloss acceptor, length scratch dirt is more conspicuous. It is necessary to offer the pigment system ink constituent which can be used for the front face of an ink jet acceptance element printing the image which has the endurance and dirt-proof nature which were improved.

[0016] Generally ozone exists by the concentration of 10 – 50 PPB in the air in a sea level. An ozone level exceeds such level only under specific conditions. However, even in a low ozone level, when permeability is high, an ink jet color, colors, such as an ink jet pigment, and a pigment have very high susceptibility (for example, when printed by the porosity gloss acceptor), and fade sharply.

[0017] The ink jet acceptor designed for outdoor-type ways will fade sharply, if they are also exposed to ozone with high permeability, although there is an inclination to have good endurance when printed in pigment system ink.

[0018] A U.S. Pat. No. 5,716,436 specification and provisional publication of a patent In the 2000 No. -290553 official report, using a water-dispersion polymer in the ink jet ink printed by the regular paper is indicated. However, the image printed using these ink has low optical density, and its humid-proof abrasiveness is very inadequate, and it will not bear an outdoor-type way.

[0019] British ***** 2 351 292 No. is related with the ink jet ink constituent containing the water dissipation nature polymer which comes to contain a resultant. However, using these constituents on acceptors other than a regular paper is not indicated by this patent.

[0020]

[Problem(s) to be Solved by the Invention] The purpose of this invention is offering the ink jet printing approach which uses the ink jet ink constituent containing a water-dispersion polymer, and the image printed by the front face of an ink jet acceptance element using this ink constituent has the ozone proof fastness and physical endurance (for example, scratch-proof nature and dirt-proof nature) which were improved.

[0021]

[Means for Solving the Problem] The process which prepares the ink jet printer with which these purpose and other purposes answer A digital data signal, B) The process loaded with the ink acceptance element which comes to contain the base material which is supporting the ink absorbing layer of the porosity which has the continuous and same breadth which has a continuation void in the above-mentioned printer, C) The process which loads said printer with water, a wetting agent, a pigment, and the ink jet ink constituent that comes to contain the particle of a water-dispersion polymer, It is attained by this invention about the ink jet printing approach including the process which answers the D aforementioned digital data signal at a list, and is printed on said ink absorbing layer using said ink jet ink.

[0022] The image which has the ozone proof fastness and physical endurance (for example, scratch-proof nature and dirt-proof nature) which were improved by the ink jet printing approach of this invention which uses a porosity acceptor and the ink constituent containing the particle of a water-dispersion polymer is offered.

[0023]

[Embodiment of the Invention] The base material for the ink acceptance element used in this

invention paper, resin coat paper, and plastics (for example, polyolefine type resin or polyester type resin (for example, polyethylene terephthalate) — Polycarbonate resin, polysulfone resin, methacrylic resin, cellophane, Acetate plastics, diacetyl cellulose, a cellulose triacetate, vinyl chloride resin, Polyethylenenaphthalate, polyester diacetate, various glass ingredients, etc. may include open pore structure (for example, thing made from polyolefine or polyester). The thickness of the base material used in this invention is 12 to 500 micrometer. It is 75 to 300 micrometer preferably. It can carry out.

[0024] the desirable voice of this invention — like — setting — the above — the ink absorbing layer of porosity with the continuous and same breadth contains the organic particle or the inorganic particle. A core / shell particle (for example, the [of Kapusniak for which it applied on June 30, 2000 / United States patent application] thing currently indicated in 09 / No. 609/969 specification), and a homogeneity particle (for example, thing currently indicated in the Europe ***** No. 0120331.3 specification) are contained in the example of the organic particle which may be used.

[0025] Acrylic resin, styrene resin, a cellulosic, polyvinyl resin, an ethylene-allyl compound copolymer, and a polycondensation polymer (for example, polyester) are contained in the example of the organic particle which may be used.

[0026] A silica, an alumina, a titanium dioxide, clay, a calcium carbonate, a barium sulfate, or a zinc oxide is contained in the example of the inorganic particle which may be used in this invention.

[0027] the desirable voice of this invention — like — setting — the above-mentioned porosity ink absorbing layer — 20% - 100% of particle, and 0% - 80% of giant-molecule binder — it comes to contain 80% - 95% of particle, and 20% - 5% of giant-molecule binder preferably the above-mentioned giant-molecule binder — a hydrophilic polymer (for example, polyvinyl alcohol —) A polyvinyl pyrrolidone, gelatin, cellulose ether, poly oxazoline, a polyvinyl acetamide and Pori hydrolyzed partially (vinyl acetate-co-vinyl alcohol) Polyacrylic acid, polyacrylamide, polyalkylene oxide, sulfonation or the polyester by which phosphorylation was carried out, and polystyrene, casein, a zein, albumin, a chitin, chitosan, a dextran, pectin, a collagen derivative, koro JIAN (collodian), an agar, an arrowroot, a gar, carrageenan, tragacanth, xanthene, and Lamb Sun (rhamsan) etc. — you may be. Preferably, the above-mentioned hydrophilic polymers are polyvinyl alcohol, hydroxypropylcellulose, the hydroxypropyl methylcellulose, polyalkylene oxide, a polyvinyl pyrrolidone, polyvinyl acetate, these copolymers, or gelatin.

[0028] In order to give mechanical endurance to an ink jet record element, little addition of the cross linking agent which acts on the binder considered above may be carried out. Such an additive improves the bonding strength of a layer. For example, cross linking agents, such as a carbodiimide, a multi-functional value aziridine, an aldehyde, isocyanate, epoxide, a polyvalent metal cation, a vinyl sulfone, pyridinium, the pilus JIRIUMU (pyridylum) dication ether, a methoxy alkyl melamine, triazine, a dioxane derivative, chromium alum, and a sulfuric-acid zirconium, can be used. Preferably, a cross linking agent is an aldehyde, an acetal, or ketal (for example, 2, 3-dihydroxy -1,4-dioxane).

[0029] A porosity ink jet acceptance layer usually comes to contain the inorganic particle or the organic particle combined together with the binder as used in this specification. The amount of the particle in this type of coating is over critical particle volume concentration far in many cases, consequently the porosity rate of coating becomes high. In the ink jet printing approach, a liquid ink drop is absorbed quickly during coating by capillary action, and an image is in a set-to-touch condition immediately after coming out of a printer. Therefore, by porosity coating, quick "desiccation" of ink becomes possible and the image which has dirt-proof nature arises.

[0030] Moreover, the above-mentioned porosity ink absorbing layer can also contain open pore polyolefine, open pore polyester, or the open pore film. The open pore film can be made to form by known technique called phase inversion. the example of the porosity ink absorbing layer which comes to contain the open pore film — the Europe patent application 01202701.No. 7 — and — said — it is indicated in each specification of No. 01202711.6.

[0031] Independent or the organic pigment put together, and an inorganic pigment (for example, U.S. Pat. No. 5,026,427, ** No. 5,086,698, ** No. 5,141,556, ** No. 5,160,370 and ** what is indicated in each specification of No. 5,169,436) are contained in the pigment which may be used in this invention. It will depend for strict selection of a pigment on a specific application and engine-performance requirements (for example, color reproduction and image stability). To the suitable pigment for the

use in this invention, for example, an azo pigment, a monoazo pigment, A disazo pigment, an azo pigment lake, a beta-naphthol pigment, the Naphthol AS pigment, A benzoimidazolone pigment and iso indoline (isoindoline) Pigment, A polycyclic type pigment, a phthalocyanine pigment, a quinacridone pigment, a perylene pigment, and a peri non pigment, A thioindigo pigment, an anthra pilus MIDON pigment, a flavanthrone pigment, Carbon black is contained in an anthanthrone (anthanthrone) pigment, a dioxazine pigment, a thoria reel carbonium pigment, a kino FUTARON pigment, a diketo pyrrolo pyrrole pigment, a titanium dioxide, ferrous oxide, and a list.

[0032] For the example of a type of the pigment which may be used A Color Index The pigment yellow 1, 2, 3, 5, 6, 10, 12, 13, 14, 16, 17, 62, 65, 73, 74, 75, 81, 83, 87, 90, 93, 94, 95, 97, 98, 99, 100, 101, 104, 106, 108, 109, 110, and 111, (C. I.) 113, 114, 116, 117, 120, 121, 123, 124, 126, 127, 128, 129, 130, 133, 136, 138, 139, 147, 148, 150, 151, 152, 153, 154, 155, 165, 166, 167, 168, 169, 170, 171, 172, 173, 174, 175, 176, 177, 179, 180, 181, 182, 183, 184, 185, 187, 188, 190, 191, 192, 193, 194; C.I. pigment Orange 1, 2, 5, 6, 13, 15, 16, and 17, 17: 1, 19, 22, 24, 31, 34, 36, 38, 40, 43, 44, 46, 48, 49, 51, 59, 60, 61, 62, 64, 65, 66, 67, 68, the 69; C.I. pigment red 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, and 14, 15, 16, 17, 18, 21, 22, 23, 31, 32, 38, 48:1, 48:2, 48:3, 48:4, 49:1, 49:2, 49:3, 50:1, 51, 52:1, 52:2, 53:1, 57:1, 60:1, 63:1, 66, 67, 68, 81, 95, 112, 114, 119, 122, 136, 144, 146, 147, 148, 149, 150, 151, 164, 166, 168, 169, 170, 171, 172, 175, 176, 177, 178, 179, 181, 184, 185, 187, 188, 190, 192, 194, 200, 202, 204, 206, 207, 210, 211, 212, 213, 214, 216, 220, 222, 237, 238, 239, 240, 242, 243, 245, 247, 248, 251, 252, 253, 254, 255, 256, 258, 261, 264; C. I. pigment violet 1, 2, and 3, 5: 1, 13, 19, 23, 25, 27, 29, 31, 32, 37, 39, 42, 44, the 50; C.I. pigment blues 1, 2, 9, 10, 14, 15:1, 15:2, 15:3, 15:4, 15:6, 15, 16, 18, and 19, 24: 1, 25, 56, 60, 61, 62, 63, 64, 66; C. I. pigment Green 1, 2, 4, 7, 8, 10, and 36, the 45; C.I. pigment blacks 1, 7, 20, 31, and 32, and C.I. pigment Brown 1, 5, 22, 23, 25, 38, 41, and 42 are contained.

[0033] The pigment used in the desirable mode of this invention is the C.I. pigment blue 15:3, the C.I. pigment red 122, the C.I. pigment yellow 155, the C.I. pigment yellow 74, and a screw. (free-wheel-plate ROSHIA nil alumino) They are tetra-phenyl disiloxane or the C.I. pigment black 7.

[0034] The aqueous dispersion medium for the ink constituent used in this invention is the mixture of water or water, and at least one sort of water miscibility auxiliary solvents. It depends for selection of suitable mixture on a specific application (for example, the drying time of the ink jet ink in which desired surface tension and viscosity, the pigment chosen, and the pigment were added, the type of the paper in which ink is printed by the list). For the example of representation of the water miscibility auxiliary solvent which can be chosen (1) — alcohol (for example, methyl alcohol, ethyl alcohol, and n-propyl alcohol —) Isopropyl alcohol, n-butyl alcohol, sec butyl alcohol, T-butyl alcohol, isobutyl alcohol, furfuryl alcohol, and tetrahydrofurfuryl alcohol, (2) ketones, or keto alcohol (for example, an acetone —) A methyl ethyl ketone and diacetone alcohol, (3) ether (for example, a tetrahydrofuran and dioxane), (4) — ester (for example, ethyl acetate, ethyl lactate, and ethylene carbonate —) and propylene carbonate and (5) polyhydric alcohol (for example, ethylene glycol —) A diethylene glycol, triethylene glycol, tetraethylene glycol, Propylene glycol, a polyethylene glycol, glycerol, 2-methyl -2, 4-pentanediol, the low-grade alkyl mono-ether guided from 1, 2, 6-hexane triol and a thioglycol, and (6) alkylene glycol, and a low-grade alkyl diether (for example, the ethylene glycol monomethyl (or ethyl) ether —) The diethylene-glycol monomethyl (or ethyl) ether, the diethylene-glycol monobutyl (or ethyl) ether, The propylene glycol monomethyl (or ethyl) ether, polyethylene-glycol butyl ether, The triethylene glycol monomethyl (or ethyl) ether and the diethylene-glycol dimethyl (or ethyl) ether, (7) — a nitrogen content cyclic compound (for example, a pyrrolidone and an N-methyl -2-pyrrolidone —) And 1, 3-dimethyl (8) sulfur content compound (for example, dimethyl sulfoxide, 2, and 2'-thiodiethanol and a tetramethylen sulfone) is contained in -2-imidazolidinone and a list.

[0035] Generally it is desirable to make pigment system ink jet ink from the form of a thick mill grinding object, and this is diluted by behind suitable concentration to use it in an ink jet printing system. This technique enables it to prepare a lot of pigment system ink from equipment. When the above-mentioned mill grinding object is made in a solvent, it is diluted with water and other solvents in option, and it considers as suitable concentration. When the above-mentioned mill grinding object is made underwater, it is diluted with the further water or a water miscibility solvent, and it considers as desired concentration. Ink is adjusted to each viscosity desirable for an application, color, hue, saturated concentration, and printing field coating weight by dilution. About the preparation approach

of a mill grinding object, they are U.S. Pat. No. 5,679,138 and **. No. 5,670,139 and **. It is indicated in each specification of No. 6,152,999. It is added by the ink jet ink constituent, and it is used for destroying a pigment in submicron magnitude in a grinding process, a colloid dispersing element is maintained at stability over a long period of time, and it is made for a dispersant not to have condensation in the desirable mode of this invention, either.

[0036] in the case of an organic pigment, ink can contain the pigment which attains to about 30 mass % — although kicked — general — almost all the ink jet printing application — setting — all ink constituents — about — 0.1 to 10 mass % — desirable — it is in the range of 0.1 – 5 mass % — I will come out. Generally, when an inorganic pigment is chosen, since an inorganic pigment has specific gravity higher than an organic pigment, ink tends to contain the pigment of higher mass %, and may serve as about 75% of high content from the equivalent ink which uses an organic pigment depending on the case.

[0037] the amount of the aqueous dispersion medium used — the total mass of ink — receiving — about 70 to 99 mass % — it is in the range of about 90 to 98 mass % preferably. The mixture of water and polyhydric alcohol (for example, diethylene glycol) is useful as an aqueous dispersion medium. In a desirable mode, ink contains the water miscibility solvent of 5 – 60 mass %. A percentage receives the total mass of an aqueous dispersion medium.

[0038] the particle of the water-dispersion polymer used in this invention — general — 1 micrometer the following — desirable — 0.5 micrometers the following — more — desirable — 0.25 micrometers It has the mean particle diameter of the following.

[0039] Generally the water-dispersion polymer used in this invention may be a hydrophobic polymer of which [which may be stabilized in an aqueous medium] presentation. Generally such a hydrophobic polymer is classified into either a condensation polymer or an addition polymer. Polyester, a polyamide, polyurethane, poly urea, a polyether, a polycarbonate, many acid anhydrides, and the polymer that comes to contain the combination of an above-mentioned type are contained in a condensation polymer. An addition polymer is the polymer formed of the polymerization of a monomer vinyl type [, such as the ester guided from an allyl compound, vinyl ether, a vinyl heterocyclic compound, styrene an olefin and a halogenation olefin, ethylene system unsaturated carboxylic acid, and them, partial saturation nitril, vinyl alcohol, acrylamide and methacrylamide, a vinyl ketone, and a multi-functional value monomer,], or a copolymer formed from the various combination of these monomers.

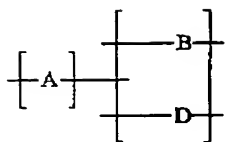
[0040] The styrene / acrylic polymer prepared according to the radical polymerization of the vinyl monomer in the inside of an aqueous emulsion are contained in the 1st class of desirable water-dispersion polymer. The suitable monomer for this styrene / acrylic polymer may be set to the technical field concerned, and is known as indicated for example, in the U.S. Pat. No. 5,594,047 specification. In the desirable mode of this invention, the monomer for this styrene / acrylic polymer is the ester of an acrylic acid, the ester of a methacrylic acid, styrene, or a styrene derivative.

[0041] For example, the monomer for above-mentioned styrene / acrylic polymer A methyl methacrylate, ethyl methacrylate, methacrylic-acid butyl, an ethyl acrylate, Butyl acrylate, acrylic-acid hexyl, acrylic-acid n-octyl, Methacrylic-acid lauryl, 2-ethylhexyl methacrylate, acrylic-acid nonyl, Methacrylic-acid benzyl, 2-hydroxypropyl methacrylate, acrylonitrile, A methacrylonitrile, vinyl acetate, propionic-acid vinyl, a vinylidene chloride, A vinyl chloride, styrene, t-butyl styrene, vinyltoluene, a butadiene, An isoprene, N,N-dimethylacrylamide, an acrylic acid, a methacrylic acid, Chloro methacrylic-acid, maleic-acid, allylamine, N, and N-diethyl allylamine, A vinyl sulfonamide, acrylic-acid sodium, sodium methacrylate, Acrylic-acid ammonium, methacrylic-acid ammonium, acrylamide propane-chlorination triethyl ammonium, Methacrylamide propane-chlorination triethyl ammonium, hydrochloric-acid vinylpyridine, Vinyl sodium phosphonate and 1-methylvinyl sodium phosphonate, Sodium vinylsulfonate, 1-methylvinyl sulfonic-acid sodium, 2-acrylamide -2-methyl It can be made to form from -1-propane sulfonic-acid sodium or styrene sulfonic-acid sodium.

[0042] An aqueous dispersibility polyester ionomer is contained in the 2nd class of water-dispersion polymer which may be used in this invention. In a desirable mode, these polyester ionomers have the following structures.

[0043]

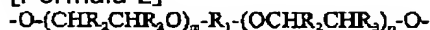
[Formula 1]



[0044] It is the residue of one or more sorts of diol components which become together and come to contain A, and 100-mol % of a repeating unit among an upper type, and is expressed by the following structures.

[0045]

[Formula 2]

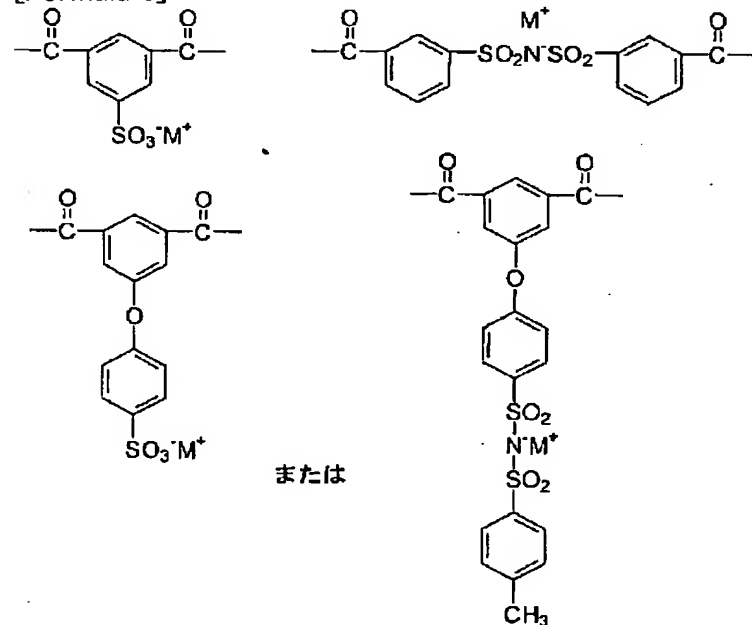


[0046] the inside of an upper type, and m and n — independent — the integer of 0-4 — expressing —
 - R1 The alkylene group which has 5 and 1-16 carbon atoms, the cyclo alkylene group which has 5-20 carbon atoms, The cyclo bis-alkylene group which has 8-20 carbon atoms, the bicyclo alkylene group which has 7-16 carbon atoms, or a tricyclo alkylene group, The bicyclo bis-alkylene group or tricyclo bis-alkylene group which has 9-18 carbon atoms, The arylene radical which has the arene bis-alkylene group which has 8-20 carbon atoms, or 6-12 carbon atoms, The poly dimethylsiloxane segment which has a carbitol end group is expressed, and it is R2. And R3 The aryl group which is not permuted [the permutation which has the alkyl group which is not permuted / the permutation which has H and 1-6 carbon atoms, or /, or 6-12 carbon atoms, or] is expressed independently respectively.

[0047] B is the residue of the diacid component which comes to contain 8-50-mol % of a repeating unit, and is expressed by one or more sorts of the following structures.

[0048]

[Formula 3]

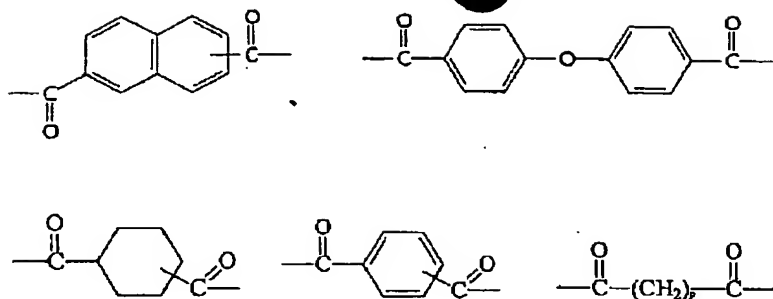


[0049] The inside of an upper type, and M+ Alkali metal (for example, Li, Na, and K), ammonium, a phosphonium (for example, ammonium, methylammonium, triethyl ammonium, tetra-alkylammonium, aryl trialkylammonium, etc.) radical (for example, triphenyl phosphonium, tetrabutyl phosphonium), complex aromatic series ammonium (for example, pyridinium, imidazolium, and N-methylammonium), a sulfonium radical, a GUANIDIUM radical, a friend JINIUM radical, etc. are expressed.

[0050] D is the residue of the diacid component which comes to contain 50-92-mol % of a repeating unit, and is expressed by one or more sorts of the following structures.

[0051]

[Formula 4]



または

[0052] p expresses the integer of 2-12 among an upper type.

[0053] In the typical diol which A in the above-mentioned formula expresses Ethylene glycol, a diethylene glycol, triethylene glycol, Thiodiethanol, cyclohexane dimethanol, bisphenol A, Transformer -1, 4-cyclohexane diol, dodecane diol, Cis- - EKISO -2, 3-norbornane diol, 5-norbornene -2, 2-dimethanol, Hydroquinone screw (2-hydroxy ethyl ether) (Gelest Inc.) The poly dimethylsiloxane (MW=1000 (DMS-C15)) which has a carbitol end group is contained.

[0054] In this invention, Eastman AQ (trademark) polyester (Eastman Chemical Company) is contained in the example of useful water-dispersion polyester. Eastman polyester, AQ 29 (trademark), and AQ 38 (trademark) — and — AQ 55 (trademark) comes to contain isophthalic acid [of a different amount], sulfoisophtharic acid sodium, diethylene-glycol and 1, and 4-cyclohexane dimethanol. These thermoplastic amorphous ionicity polyester is prepared by an elevated temperature and low-pressure melting phase condensation polymerization, and this melting product is extruded by the small pellet. The minimum churning distributes easily in 70-degree C water, and this solid-state polymer produces the translucent hypoviscosity dispersing element which does not contain the further surfactant or the further solvent at all. By changing the amount of an ionicity monomer (namely, sulfoisophtharic acid), particle size is controllable. Particle size is 0.02 to 0.1 micrometer. It migrates to the range.

[0055] Aqueous dispersibility polyurethane is contained in the 3rd class of water-dispersion polymer which may be used in this invention. The example of useful polyurethane is indicated in the Europe patent application 01201186.No. 2 specification. These ingredients are "Polyurethane Handbook", Hanser Publishers, Munich Vienna, and 1985. It can prepare as indicated. The example of aqueous dispersibility polyurethane is Witco Corp. It depends. A Witcobond (trademark) polyurethane dispersing element and BF Goodrich Company It depends. It is Sancure (trademark) polyurethane.

[0056] A polyurethane-acrylic polymer alloy is contained in the 4th class of water-dispersion polymer which may be used in this invention. The example of a useful polyurethane-acrylic polymer alloy dispersing element is indicated in the U.S. Pat. No. 5,173,526 specification. The example of this type of ingredient is based on CK Witco Corporation. It is Witcobond A-100 and this is an aliphatic series polyester alloy which uses urethane and polyacrylate as the base.

[0057] the water-dispersion polymer used in this invention — the inside of ink jet ink — general — 0.1 to 10 mass % — desirable — 0.5-5 mass % existence of is done.

[0058] Generally, in the printing field after these ink was printed, it was admitted by adding a water-dispersion polymer particle in ink that the gloss level of the front face of an acceptor could be raised.

[0059] Generally a jet rate, the separation length of a drop, the magnitude of a drop, and the stability of flow are influenced with the surface tension and viscosity of ink. Suitable pigment system ink jet ink to use it with an ink jet printing system should have the range of 20×10^{-5} - 60×10^{-5} N/cm (20 - 60 dyn/cm), and the surface tension which is in the range of 30×10^{-5} - 50×10^{-5} N/cm (30 - 50 dyn/cm) more preferably. Control of the surface tension in water color ink is attained by addition of a little surfactant. A simple trial-and-error experiment can determine the amount of the surfactant which should be used. U.S. Pat. No. 5,324,349, ** No. 4,156,616 and ** An anionic surface active agent and a cationic surface active agent can be chosen from other surface active agents known in the ink jet ink technical field by the thing list currently indicated in each specification of No.

5,279,654. Surfynol (trademark) of the product [surfactant / commercial] made from Air Products, and product made from DuPont Product made from Zonyl (trademark) and 3M Fluorad (trademark) is contained.

[0060] A wetting agent is used for the constituent used in the approach of this invention in order to help to prevent ink's hardening by drying or solidifying in the orifice of an ink jet print head. It sets to the constituent used in this invention for this purpose, and they are ethylene glycol, a diethylene glycol, triethylene glycol, propylene glycol, tetraethylene glycol, a polyethylene glycol, glycerol, and 2-methyl in a useful polyhydric-alcohol wetting agent. -2, 4-pentanediol, 1 and 2, 6-hexane triol, and a thioglycol are contained. A wetting agent can be used by the concentration of 10 - 50 mass %. In a desirable mode, the mixture of a diethylene glycol, or a glycerol and a diethylene glycol is used by the concentration of 10 - 20 mass %.

[0061] the above-mentioned ink has the physical property which suits an extensive radiation condition (namely, the drive frequency of the piezoelectric device in either the driver voltage in a thermal ink jet airline printer and pulse width, drop-on-demand type equipment or continuous system equipment and a list — the configuration of a nozzle, and magnitude).

[0062] Moreover, you may help to divide, when acceptor material is the paper to which sizing processing was performed highly, and to add a penetrating agent (zero to 10 mass %) to the ink constituent used in the approach of this invention, and for ink to permeate acceptor material. Concentration with a final penetrating agent desirable in the ink used in this invention is n-propanol of 1 - 6 mass %.

[0063] Moreover, a destruction-of-life agent (0.01 - 1.0 mass %) may be added to the ink constituent used in the approach of this invention, and growth of the microorganism which may be generated in ink by the passage of time and which is not desirable may be prevented. The last concentration of a destruction-of-life agent desirable in the ink used in this invention is Proxel(trademark) GXL of 0.05 - 0.5 mass % (Zeneca Colours Co.). A thickener, a conductive enhancement agent, a Kogation inhibitor, a drying agent, and a defoaming agent are contained in the further additive which may exist in option in ink jet ink.

[0064] The ink jet ink manufactured using the water-dispersion polymer used in this invention is used in ink jet printing applied to ink acceptor material in the format by which the liquid liquid ink drop was controlled by injecting a liquid ink drop from two or more nozzles (or orifice) which can be set to the print head of an ink jet printer.

[0065] How many differ is used for a commercial ink jet printer, and it is controlling adhesion of a liquid ink drop. Generally as such an approach, there are two kinds of types, a continuous-flow type and a drop-type on demand.

[0066] In a drop-on-demand type system, the drop of ink is directly injected from an orifice in one location of an ink absorbing layer with the piezoelectric device controlled according to a digital data signal, sound equipment, or the pressure generated by thermal **. A liquid ink drop is not generated until it is needed, and it is not injected from the orifice of a print head. The ink jet printing approach (and related printer) is marketed, and does not have the need of explaining to a detail.

[0067] The following examples explain the usefulness of this invention.

[0068]

[Example] The one or less-example pigment dispersing element was prepared.

[0069]

Magenta pigment dispersing element (MD-1) Mill grinding object 325 g Giant-molecule bead (average diameter = 50 micrometers)

(Tumbling media)

Quinacridone Magenta made from Sun Chemical Co. 30 g (pigment red 122)

Oleyl methyl taurine (OMT) potassium salt 9 g Deionized water 208 g Proxel GXL (trademark) 0.2g (destruction-of-life agent made from Zeneca)

[0070] the high energy medium mill manufactured by Morehouse-Cowles Hochmeyer in the above-mentioned component — using it — BYK-Gardner from — it ground in the obtained 2l. double-wall container. This mill was operated in the room temperature for about 8 hours. VWR Scientific Products from — obtained 4-8 micrometers By filtering the above-mentioned mill grinding object with a KIMAX (trademark) Buchner funnel, this dispersing element was separated from tumbling

media.

[0071] a cyanogen pigment dispersing element (CD-1) — this dispersing element — instead of [of a Magenta pigment] — screw (free-wheel-plate ROSHIA nil alumino) Except for having used tetraphenyl disiloxane (Eastman Kodak Co.) and having used 18g OMT, it prepared like the above-mentioned Magenta pigment dispersing element.

[0072] a yellow pigment dispersing element (YD-1) — this dispersing element was prepared like the above-mentioned Magenta pigment dispersing element except for having used the pigment yellow 74 (Clariant Corporation) instead of the Magenta pigment, and having used 3.75g OMT.

[0073] the preparation polyester dispersing element 1 (PE-1) mechanical agitator of a water-dispersion polymer, an effective reflux condenser, and N2 It had the inlet. the 3 opening round bottom flask of 500mL — 5-sulfoisophtharic acid sodium of 28.96 g, isophthalic acid of 81.74 g, and the diethylene glycol of 45.37 g — and — It loaded with 46.51g cyclohexane dimethanol. It is this flask Slight N2 It placed into the salt bath of 220 degree C, agitating slowly under an air current. It is 0.51g when a reaction mixture dissolves. Fascat 4100 (trademark) catalyst is added and it is a polymerization. When it was made to go on for 8.0 hours, the water of the amount of theory was distilled off. It is this copolymer N2 It cooled radiationally under the ambient atmosphere, next this polymer was taken out from the flask.

[0074] It had the mechanical agitator and the reflux condenser. The 3 opening round bottom flask of 250mL was loaded with the deionized water of 80mL, and it heated at 85 degrees C. Agitating quickly, the 20.3g above-mentioned polyester ionomer was added gradually, and this dispersing element was heated in 85 degrees C for 2 hours. Heating was set by the stop, this dispersing element was set to the room temperature, and it agitated all night. This mixture was filtered and 92.5g of dispersing elements containing the polymer of 18.7 mass % which bloomed cloudy slightly was obtained.

[0075] a polyester dispersing element 2 (PE-2) mechanical agitator, an effective reflux condenser, and N2 It had the inlet. the 3 opening round bottom flask of 500mL — 5-sulfoisophtharic acid sodium of 28.96 g, isophthalic acid of 81.74 g, and the diethylene glycol of 41.72 g — and — It loaded with 42.77g cyclohexane dimethanol. It is this flask Slight N2 It placed into the salt bath of 220 degree C, agitating slowly under an air current. It is 0.49g when a reaction mixture dissolves. Fascat 4100 (trademark) catalyst is added and it is a polymerization. When it was made to go on for 8.0 hours, the water of the amount of theory was distilled off. It is this copolymer N2 It cooled radiationally under the ambient atmosphere, next this polymer was taken out from the flask.

[0076] It had the mechanical agitator and the reflux condenser. The 3 opening round bottom flask of 250mL was loaded with the deionized water of 80mL, and it heated at 85 degrees C. Agitating quickly, the 20.1g above-mentioned polyester ionomer was added gradually, and this dispersing element was heated in 85 degrees C for 2 hours. Heating was set by the stop, this dispersing element was set to the room temperature, and it agitated for 20 hours. This mixture was filtered and 90.0g of dispersing elements containing the polymer of 19.1 mass % which bloomed cloudy slightly was obtained.

[0077] Polyester dispersing element 3 (PE-3) solid An AQ-55 polyester ionomer is purchased from Eastman Chemical, next it adds in water, heating and agitating, and is the concentration of 30% of solid content. AQ-55 dispersing element was obtained.

[0078] the start raw material which used the polyester dispersing element 4 (PE-4) polyester dispersing element 4 — 164.29g 1 and 4-cyclohexane dicarboxylic acid, sulfoisophtharic acid sodium of 46.30 g, and cyclohexane dimethanol of 90.24 g — and — 61.47g Except for having considered as 1 and 10-Decan diol, it prepared according to the same procedure as the polyester dispersing element 2.

[0079] it had polyurethane dispersing element 1 (PU-1) agitator, the nitrogen inlet, and the condenser the flask of 500mL — 148.12g sulfoisophtharic acid sodium and 530.00g Tone (trademark)0200 (poly caprolactone polyol available from Union Carbide, molecular weight 530) — and — It loaded with the titanium (IV) isopropoxide of 200 ppm. It is this mixture, agitating. It heated at 250 degrees C. It is temperature when this mixture becomes transparence (about 2 hours). It raised to 270 degrees C and maintained for further 2 hours. When about 15.8g methanol condensates are collected, under [all / what / was completed mostly / an ester interchange]. It was used without having put this resultant (it being henceforth called SIP-diol) into the bottle, and refining it further.

[0080] a thermometer, an agitator, a water condenser, and the 2l. resin flask equipped with

evacuation opening are loaded with 245.48g (0.19 mols) SIP-diol — in 100 degree C, it dehydrated under reduced pressure. This flask was placed into the bath by which temperature control was carried out. reduced pressure is solved and it sets at 40 degrees C — it added in the reaction flask, agitating 54.79g (0.24 mols) bisphenol A, 64.89g (0.72 mols) 1,4-butanediol, 2-butanone of 150g, and 40 drops of dibutyl tin JIRAU rates (catalyst). Temperature was raised to 82 degrees C, the homogeneous solution was obtained, and it cooled at 70 degrees C, then 226.74g (1.02 mols) isophorone diisocyanate and 10g 2-butanone were added.

[0081] Adjusted temperature, returned to 82 degrees C, maintained for 16 hours, the reaction was made to complete, and the final polyurethane which contains isolation isocyanate only less than 3% was obtained. The content of isolation isocyanate was supervised by infrared spectroscopy measurement of the absorption peak of the place of the wave number 2240. 2000g water was added under the high shear in this reaction flask, and the stable aqueosity dispersing element was made to form. By heating under reduced pressure, 2-butanone was removed and the aqueosity dispersing element of 40% of solid content was obtained.

[0082] Tone(trademark) 0260 (the poly caprolactone polyol available from Union Carbide, molecular weight 3000) of 123.0 g (0.041 mols) was put into polyurethane dispersing element 2 (PU-2) thermometer, the agitator, the water condenser, and the 2l. resin flask equipped with evacuation opening. This was dehydrated under reduced pressure in 100 degree C. Reduced pressure was solved, and the following were added, agitating in 40 degrees C. 22.70g (0.166 mols) dimethylol propionic acid, bisphenol A of 50.90 g (0.241 mols), 1,4-butanediol of 63.58 g (0.706 mols), 2-butanone of 180 g, and 20 drops of dibutyl tin JIRAU rates (catalyst). Raised temperature to 82 degrees C, maintained for 16 hours, the reaction was made to complete, and the intermediate field which contain isolation isocyanate only less than 3% were obtained.

[0083] The content of isolation isocyanate was supervised by infrared spectroscopy measurement of the absorption peak of the place of the wave number 2240. This reaction mixture was diluted with the 75g tetrahydrofuran, 19.7g of 45% of pottasium hydroxide solution neutralized, and 95% of theoretical ionization was attained to dimethylol propionic acid. Add 1300g distilled water under a high shear into this neutralized mixture, and made the stable aqueosity dispersing element form, then it was made to evaporate under reduced pressure, and 2-butanone was removed.

[0084] The polyurethane dispersing element 3 (PU-3) polyurethane dispersing element 3 prepared the used start raw material like the polyurethane dispersing element 2 except for having considered as 2 and 2-oxy-JIETA (dimethylol-propionic-acid [of 51.6g KM101733 (the polycarbonate polyol made from Stahl Co., m.w.860), and 10.20 g], and 10.0g) Norian, 1,4-butanediol of 24.33 g, and 111.20g isophorone diisocyanate.

[0085] Pori acrylic dispersing element 1 (PA-1)400g deionized water — and — The 1l. 3 opening round bottom flask equipped with the mechanical agitator and the nitrogen inlet was loaded with Olin 10G (trademark) 0.6g surfactant. In the thermostatic bath, this solution was purged for 30 minutes with nitrogen, and was heated at 80 degrees C. a 172.8g methyl acrylate — and — 7.2g 2-acrylamide -2-methyl -1-propane sulfonic acid (sodium salt) was added, and it agitated for 3 minutes. 16.4g 10% sodium persulfate solution — and — The sodium-metabisulfite solution was added 10 5.5g%, and the polymerization was made to start. The polymerization was continued for 1 hour and it heated in 80 degrees C for further 1 hour. Temperature was lowered to 65-70 degrees C, and adding after mixing of t-butyl butyl hydroperoxide (10%) and the formaldehyde-sodium hydrogensulfite (10%) of 1mL was carried out respectively. This latex was cooled and filtered. This dispersing element contained the solid content of 30 mass %.

[0086] the Pori acrylic dispersing element 2 (PA-2) Pori acrylic dispersing element 2 — monomer mixture — methacrylamide of 14.17 g, the butyl acrylate of 106.2 g, and 2-acrylamide of 14.17 g -2-methyl -1-propane sulfonic acid (sodium salt) — and — The surfactant which should consist of 45.36g styrene and was used was prepared like the Pori acrylic dispersing element 1 except for having considered as sodium lauryl sulfate instead of Olin 10G. This dispersing element contained the solid content of 30 mass %.

[0087] The Pori acrylic dispersing element 3 (PA-3) Pori acrylic dispersing element 3 was prepared by mixing until 66g water and 9g triethanolamine, and the above-mentioned polymer dissolve completely Jonrez [J-4655 [25g] (styrene-acrylic polymer obtained from Westvaco Corporation).

[0088] 20-degree-C heating rate for /was used for the glass transition temperature (T_g) of a polymer property glass-transition-temperature desiccation polymer ingredient, and it measured it by the differential scanning calorimetry (DSC). T_g This specification is defined as point of inflection of glass transition.

[0089] About the particle of all particle-size measurement, it is rookhaven Instruments Corporation. It was manufactured. A property decision was made by 90plus Particle Sizer. Capacity average diameters are enumerated below.

[0090] The steric exclusion chromatography (SEC) in the inside of the tetrahydrofuran which uses three Polymer Laboratories plgl (trademark) small mixing (mini-mixed) B columns analyzed the average-molecular-weight above-mentioned sample. The molecular weight distribution of the group of this column, and 580-2,300,000 proofread using the narrow polystyrene criterion.

[0091] The various above-mentioned polymer properties are summarized to the following table I.

[0092]

[Table 1]

表 I

| ポリマー分散体 | 粒径 (nm) | 乾燥ポリマー の T _g (°C) | 重量平均 分子量 |
|--------------|------------|---------------------------------|-------------|
| ポリエステル分散体 1 | 308 | 23 | 3,400 |
| ポリエステル分散体 2 | 295 | 38 | 4,125 |
| ポリエステル分散体 3 | 19.9 | 55 | 18,000 |
| ポリエステル分散体 4 | 110.2 | 6 | 10,400 |
| ポリウレタン分散体 1 | 143.2 | 44 | 5,580 |
| ポリウレタン分散体 2 | 18.0 | 80 | 17,400 |
| ポリウレタン分散体 3 | 8.2 | 71 | 20,600 |
| ポリアクリル系分散体 1 | 100 | 25 | >1,000,000 |
| ポリアクリル系分散体 2 | 86 | 0 | >1,000,000 |

[0093] The ink formulation used in preparation this invention of ink was prepared by mixing agitating all components quietly in a room temperature. pH of final mixture is addition of triethanolamine. It adjusted to 8.5. everything but a pigment and a water-dispersion polymer — the glycerol of 10 mass %, and the triethylene glycol of 23 mass % — and — 2.5 mass % Ink was made to also contain Dowanol DPM (trademark).

[0094] The pigment and water-dispersion polymer which are used for the ink list used in this invention in three sorts of ink for a comparison are shown in the following table II.

[0095]

[Table 2]

表II

| インク | ポリマー分散体 | 顔料分散体 |
|------------|------------|------------|
| G-1 (対照標準) | 無し | CD-1 (2.5) |
| G-2 (対照標準) | 無し | MD-1 (2.9) |
| G-3 (対照標準) | 無し | YD-1 (2.9) |
| I-1 | PE-1 (2.5) | CD-1 (2.5) |
| I-2 | PE-2 (2.5) | CD-1 (2.5) |
| I-3 | PE-3 (2.5) | CD-1 (2.5) |
| I-4 | PA-1 (2.5) | CD-1 (2.5) |
| I-5 | PA-2 (2.5) | CD-1 (2.5) |
| I-6 | PU-3 (2.5) | CD-1 (2.5) |
| I-7 | PE-3 (2.5) | MD-1 (2.9) |
| I-8 | PE-4 (2.5) | MD-1 (2.9) |
| I-9 | PU-2 (2.0) | MD-1 (2.9) |
| I-10 | PA-3 (2.0) | MD-1 (2.9) |
| I-11 | PE-1 (2.5) | MD-1 (2.9) |
| I-12 | PU-1 (2.0) | MD-1 (2.9) |
| I-13 | PA-3 (2.0) | YD-1 (2.9) |

[0096] The ink jet record element acceptor 1 was made into the Xerox 4024DP regular paper (reference).

[0097] The acceptor 2 was made into the porosity gloss acceptor which comes to contain two layers in the polyethylene coat paper. a bottom member — fumed alumina, Cab-O-Sperse PG003 (trademark) (Cabot Corp.), polyvinyl alcohol, and GH-23 (Nippon Ghosei) and 2, and 3-dihydroxy the thing which comes to contain — 1,4-dioxane (Clariant Corp.) with the mass ratio of 87:9:4 — carrying out — thickness — 38 micrometers ** — it carried out. a top layer — Cab-O-Sperse PG003 (trademark) (Cabot Corp.), polyvinyl alcohol, GH-23 (Nippon Ghosei), and surfactant the thing which comes to contain Zonyl FSN (trademark) (DuPont Corp.) and the mordanting ingredient MM (to refer to the following explanation) with the mass ratio of 69:6:5:20 — carrying out — thickness — 2 micrometers ** — it carried out.

[0098] MM is chlorination N-vinylbenzyl of 87 mass %. — It is the bridge formation hydrogel polymer particle which is prepared from N, N, and N-trimethylammonium and the divinylbenzene of 13 mass % and whose mean particle diameter is 80nm.

[0099] An acceptor 3 and Epson Photoglossy Paper (trademark) It was referred to as SP91001 (Epson Corporation). This is a porous gloss acceptor.

[0100] An acceptor 4 is the sake of an outdoor-type way. It considered as EI Flame Retardant Banner (Eastman Kodak Company).

[0101] The acceptor 5 was made into EI Water Resistant Self-Adhesive Vinyl for an outdoor-type way (Eastman Kodak Company).

[0102] Acceptors 2-5 are ink acceptance elements which all come to contain the ink absorbing layer of the porosity which has the continuous and same breadth on a base material.

[0103] Ink was applied to the preparation above-mentioned acceptor 2 of the applied element, and it was made to dry these elements completely in 20-degree C indoor conditions before a trial by 16.3cm³/m² (16.3 cc/m²).

[0104] Humid-proof abrasiveness and the desiccation-proof abrasiveness above-mentioned ink were applied on the above-mentioned ink jet record element. When a diameter wiped off superfluous water for the waterdrop which is about 2.54cm gently for [every] 2 minutes and after that on the front face of a sample on which ink was applied using a paper towel, the humid-proof abrasiveness trial was performed. Next, it is a diameter about the processed field like the above. On a 3.5cm field It ground against the paper towel which got dry under the pressure of 200g 8 times. The status A reflection density measured in the above-mentioned test area by the X-Rite (trademark) concentration meter was recorded, and it compared with the optical density before a trial. Humid-proof abrasiveness is defined as a percentage of the optical density (OD) held after a trial. 70% or more of humid-proof abrasiveness is desirable.

[0105] A desiccation-proof abrasiveness trial is a diameter about the above-mentioned sample. On a 3.5cm field Under the pressure of 200g, it carried out by grinding against the dry paper towel 8 times. The status A reflection density measured in the above-mentioned test area by the X-Rite (trademark) concentration meter was recorded, and it compared with the optical density before a trial. Desiccation-proof abrasiveness is defined as a percentage of the optical density (OD) held after a trial. 80% or more of humid-proof abrasiveness is desirable. About these results, it is the following table III. It enumerates.

[0106] Ozone resistance trial each sample was kept over 48 - 96 hours in the ozone chamber (amount of ozone 5 ppm, 50% of relative humidity, 21 degrees C). Before and after this ozone exposure test, it is X-Rite (trademark)414. The concentration meter was used and status A reflection density was measured. About the result of having calculated the retention (%) of status A concentration, it is the following table III. It reports. It is shown that it is so desirable that a numeric value is large, and the stability of the image to ozone exposure is more good.

[0107]

[Table 3]

表III

| インク 番号 | インク 中の ポリマー | インク 中の 顔料 | 湿潤耐久性 (濃度保持率) (%) | 乾燥耐久性 (濃度保持率) (%) | 48時間 耐オゾン堅牢度 (濃度保持率) (%) |
|-----------|-------------------|-----------------|-------------------------|-------------------------|-----------------------------------|
| C-1 | 無し | CD-1 | 57 | 52 | 29 |
| I-1 | PE-1 | CD-1 | 89 | 110 | 108 |
| I-2 | PE-2 | CD-1 | 76 | 89 | 101 |
| I-3 | PE-3 | CD-1 | 67 | 96 | 102 |
| I-4 | PA-1 | CD-1 | 94 | 106 | 104 |
| I-5 | PA-2 | CD-1 | 51 | 87 | 98 |
| I-6 | PU-3 | CD-1 | 103 | 104 | 102 |
| C-2 | 無し | MD-1 | 30 | 63 | 94 |
| I-7 | PE-3 | MD-1 | 71 | 99 | 98 |
| I-8 | PE-4 | MD-1 | 99 | 102 | 99 |
| I-9 | PU-2 | MD-1 | 90 | 100 | 99 |
| I-10 | PA-3 | MD-1 | 62 | 92 | 98 |
| C-3 | 無し | YD-1 | 73 | 68 | 100 |
| I-13 | PA-3 | YD-1 | 93 | 95 | 102 |

[0108] The above-mentioned result shows that abrasion resistance and ozone proof fastness were improved as compared with the element for a comparison in the ink containing the element and water-dispersion polymer which are using the porosity gloss acceptor 2 concerning this invention.

[0109] About a series of ink which has the component shown in two or less example, it is empty Hewlett-Packard HP 692C. It adds to an ink cartridge and is HP 692C. The printer was loaded and it printed on various acceptors. These samples were examined about humid endurance and ozone proof fastness. A result is shown in Table IV.

[0110]

[Table 4]

表IV

| 例 | ポリマー | 顔料 | 受容体 | 印刷試料の 光学濃度 | 湿潤耐久性 (濃度保持率) (%) | 96時間 耐オゾン堅牢度 (濃度保持率) (%) |
|------|------|------|-------------|---------------|-------------------------|-----------------------------------|
| C-2 | 無し | MD-1 | 1 (対照標準) | 0.94 | 紙が崩壊した | 92 |
| I-11 | PE-1 | MD-1 | 1 (対照標準) | 0.89 | 紙が崩壊した | 94 |
| I-7 | PE-3 | MD-1 | 1 (対照標準) | 0.92 | 紙が崩壊した | 88 |
| I-12 | PU-1 | MD-1 | 1 (対照標準) | 0.90 | 紙が崩壊した | 94 |
| C-2 | 無し | MD-1 | 2 | 2.41 | 18 | 91 |
| I-11 | PE-1 | MD-1 | 2 | 2.38 | 74 | 98 |
| I-7 | PE-3 | MD-1 | 2 | 2.60 | 82 | 100 |
| I-12 | PU-1 | MD-1 | 2 | 1.89 | 53 | 98 |
| C-2 | 無し | MD-1 | 3 | 2.24 | 65 | 88 |
| I-11 | PE-1 | MD-1 | 3 | 2.04 | 72 | 97 |
| I-7 | PE-3 | MD-1 | 3 | 2.28 | 94 | 99 |
| I-12 | PU-1 | MD-1 | 3 | 1.82 | 96 | 96 |
| C-2 | 無し | MD-1 | 4 | 1.30 | 100 | 84 |
| I-11 | PE-1 | MD-1 | 4 | 1.28 | 100 | 86 |
| I-7 | PE-3 | MD-1 | 4 | 1.31 | 100 | 92 |
| I-12 | PU-1 | MD-1 | 4 | 1.30 | 100 | 86 |
| C-2 | 無し | MD-1 | 5 | 1.25 | 100 | 83 |
| I-11 | PE-1 | MD-1 | 5 | 1.18 | 100 | 84 |
| I-7 | PE-3 | MD-1 | 5 | 1.19 | 100 | 92 |
| I-12 | PU-1 | MD-1 | 5 | 1.24 | 100 | 88 |

[0111] The ink in which the above-mentioned result was printed on the regular paper (acceptor 1) has low optical density, and when printed on the ink jet acceptor 2-5 to having produced the image in which endurance is inferior, it is shown that higher concentration and better endurance were accepted. Furthermore, when the ink containing a water-dispersion polymer used in this invention was used, amelioration of ozone proof fastness was accepted.

[0112] About a series of ink which has the component shown in three or less example, it is empty Hewlett-Packard HP 692C. It adds to an ink cartridge and is HP 692C. The printer was loaded and ink jet printing was carried out on the acceptor 2-5. These samples are examined about ozone proof fastness, and the result is shown in Table V.

[0113]

[Table 5]

表V

| インク | ポリマー | 顔料 | 受容体 | 96時間 耐オゾン堅牢度 (濃度保持率) (%) |
|-----|------|------|-----|-----------------------------------|
| C-1 | 無し | CD-1 | 2 | 73 |
| I-1 | PE-1 | CD-1 | 2 | 99 |
| I-2 | PE-2 | CD-1 | 2 | 98 |
| I-3 | PE-3 | CD-1 | 2 | 98 |
| C-1 | 無し | CD-1 | 3 | 61 |
| I-1 | PE-1 | CD-1 | 3 | 99 |
| I-2 | PE-2 | CD-1 | 3 | 98 |
| I-3 | PE-3 | CD-1 | 3 | 98 |
| C-1 | 無し | CD-1 | 4 | 41 |
| I-1 | PE-1 | CD-1 | 4 | 93 |
| I-2 | PE-2 | CD-1 | 4 | 91 |
| I-3 | PE-3 | CD-1 | 4 | 94 |
| C-1 | 無し | CD-1 | 5 | 49 |
| I-1 | PE-1 | CD-1 | 5 | 69 |
| I-2 | PE-2 | CD-1 | 5 | 67 |
| I-3 | PE-3 | CD-1 | 5 | 80 |

[0114] It is shown that the above-mentioned result has the ozone proof fastness containing a water-dispersion polymer by which the ink used in this invention was improved sharply.

[0115] Other desirable modes of this invention are indicated below in relation with a claim.

[0116] [1] The ink jet printer which answers A digital data signal The process loaded with the ink acceptance element which comes to contain the base material which is supporting the ink absorbing layer of the porosity which has the continuous and same breadth which has a continuation void in the process to prepare and the B aforementioned printer, C) The process which loads said printer with water, a wetting agent, a pigment, and the ink jet ink constituent that comes to contain the particle of a water-dispersion polymer, The ink jet printing approach including the process which answers the D aforementioned digital data signal at a list, and is printed on said ink absorbing layer using said ink jet ink.

[0117] [2] An approach given in [1] said water-dispersion polymer comes to contain polyester, polyurethane, or polyacrylate in.

[0118] [3] An approach given in [1] said porosity ink absorbing layer comes to contain 20% - 100% of particle, and 0% - 80% of giant-molecule binder in.

[0119] [4] An approach given in [1] said porosity ink absorbing layer comes to contain 50% - 95% of particle, and 50% - 5% of giant-molecule binder in.

[0120] [5] An approach given in [3] said particle comes to contain a silica, an alumina, a titanium dioxide, clay, a calcium carbonate, a barium sulfate, or a zinc oxide in.

[0121] [6] An approach given in [3] said whose giant-molecule binders are polyvinyl alcohol, hydroxypropylcellulose, the hydroxypropyl methylcellulose, polyalkylene oxide, a polyvinyl pyrrolidone, polyvinyl acetate, these copolymers, or gelatin.

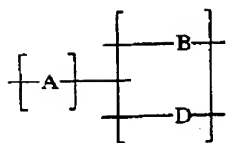
[0122] [7] An approach given in [1] in which said porosity ink absorbing layer contains the organic particle.

[0123] [8] An approach given in [1] the ink absorbing layer of porosity with the continuous and same breadth which has said continuation void comes to contain the macromolecule open pore film in.

[0124] [9] An approach given in [1] said water-dispersion polymer comes to contain a polyester ionomer in.

[0125] [10] Said polyester ionomers are the following general formulas. : [0126]

[Formula 5]



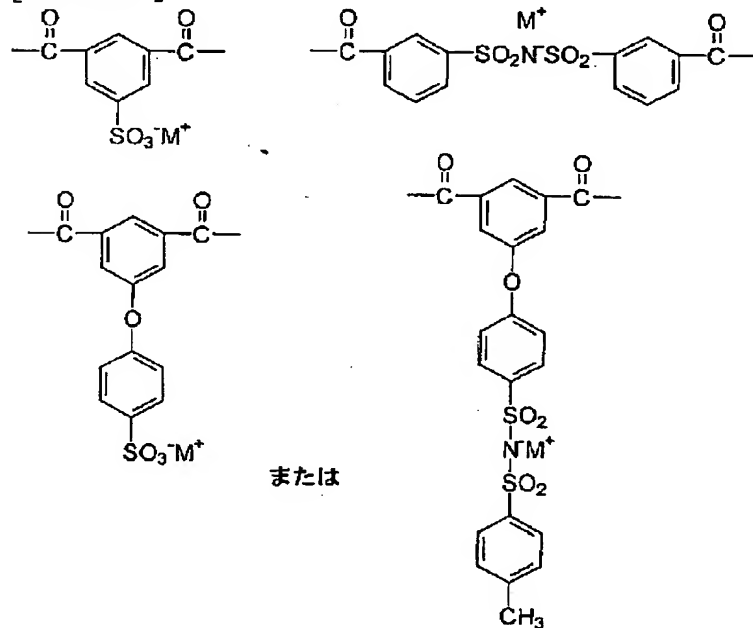
[0127] It is the residue of one or more sorts of diol components which ****, become together and come to contain A, and 100-mol % of a repeating unit among an upper type, and they are the following structures. : [0128]

[Formula 6]



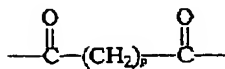
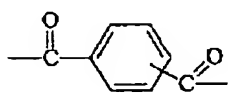
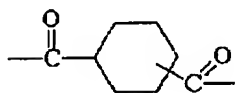
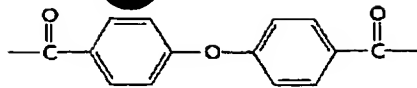
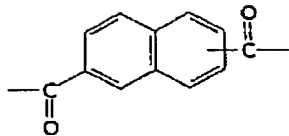
[0129] it expresses be alike — having — the inside of an upper type, and m and n — independent — the integer of 0-4 — expressing — R1 ** The alkylene group which has S and 1-16 carbon atoms, the cyclo alkylene group which has 5-20 carbon atoms, The cyclo bis-alkylene group which has 8-20 carbon atoms; the bicyclo alkylene group which has 7-16 carbon atoms, or a tricyclo alkylene group, The bicyclo bis-alkylene group or tricyclo bis-alkylene group which has 9-18 carbon atoms, The arylene radical which has the arene bis-alkylene group which has 8-20 carbon atoms, or 6-12 carbon atoms, the poly dimethylsiloxane segment which has a carbitol end group — expressing — R2 [and] And R3 Respectively, independently, it is the residue of the diacid component for which the aryl group which is not permuted [the permutation which has the alkyl group which is not permuted / the permutation which has H and 1-6 carbon atoms, or /, or 6-12 carbon atoms, or] is expressed, and B comes to contain 8-50-mol % of a repeating unit, and they are the following structures. : [0130]

[Formula 7]



[0131] It is expressed by one or more sorts of **, and they are the inside of an upper type, and M+. It is the residue of the diacid component for which alkali metal, ammonium, a phosphonium radical, complex aromatic series ammonium, a sulfonium radical, a GUANIJUMU radical, or a friend JINIUMU radical is expressed, and D comes to contain 50-92-mol % of a repeating unit, and they are the following structures. : [0132]

[Formula 8]



または

[0133] It is an approach given in [9] to which it is expressed by one or more sorts of **, and p expresses the integer of 2-12 among an upper type.

[Translation done.]

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1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

TECHNICAL FIELD

[Field of the Invention] This invention relates to the ink jet printing approach using the ink constituent containing a water-dispersion polymer.

[Translation done.]

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PRIOR ART

[Description of the Prior Art] Ink jet printing is the approach of the non-impact type which produces an image by answering a digital signal and making a liquid ink drop adhere to base materials (paper, a bright film, textile, etc.). There is an extensive application to some parts of the commercial scene covering the range from label pasting on industry to short-time printing for a desk document and pictures image formation in an ink jet printer.

[0003] In the ink jet record approach, it is required for the ink currently used to fulfill various engine-performance requirements. Generally these engine-performance requirements are severer than other liquid ink applications for writing implements (for example, a fountain pen, a felt pen, etc.) etc. Generally the following conditions are needed especially for the ink used in the ink jet printing approach.

[0004] (1) Ink should have physical properties, such as viscosity suitable for the diameter of the form of the discharge conditions (for example, driver voltage and drive frequency of a piezo oscillator) of an airline printer, and the orifice of a print head and an ingredient, and an orifice etc., surface tension, and conductivity.

[0005] (2) Ink can be kept over a long period of time, without blocking the orifice of a print head at the time of use.

[0006] (3) It is quickly fixed to ink on record media (for example, paper, a film, etc.), and the profile of the ink dot obtained becomes smooth, an ink dot inhales and picking becomes min.

[0007] (4) It should have gloss quality [the image printed] (for example, it has a clear color tone) and high and a large color gamut.

[0008] (5) The image printed should present excellent waterproof fastness (water resisting property) and color fastness to light (lightfastness).

[0009] (6) The image printed (ink) should have the good adhesive property over the front face of an image acceptance element, and should be durable, and its resistance over physical and mechanical a scratch or damage should be high.

[0010] (7) It should act on surrounding ingredients (for example, an ink storage container, a print head component part, an orifice, etc.) chemically, or should corrode, or ink should not be corroded.

[0011] (8) Ink should not be toxicity or inflammability rather than should have an unpleasant smell.

[0012] (9) Ink should present a low foaming property and high pH stability characteristics.

[0013] The ink used in various ink jet printers can be classified into either a color system or a pigment system. A color is distribution or a coloring agent by which a solvation is carried out in molecule by the dispersion medium. In a room temperature, a dispersion medium may be a liquid or may be a solid-state. The dispersion medium generally used is the mixture of water or water, and an organic auxiliary solvent. Each color molecule of each is surrounded with the molecule of a dispersion medium. In color system ink, a particle is unobservable at all under a microscope. Although there were many advances in the technique of color system ink jet ink recently, these ink usually has a fault in the paper, low optical density and poor light fastness-proof still. When using water as a dispersion medium, generally such ink also has a fault of waterproof poor robustness.

[0014] Pigment system ink is winning popularity as a means for tackling these limits. In pigment system ink, a coloring agent exists as a separate particle. These particles are processed with the additive known as the dispersant which is usually useful to controlling condensation and/or

sedimentation of a pigment particle, or a stabilizer.

[0015] Pigment system ink has a different fault from color system ink. I hear that pigment system ink carries out a different interaction from special coat paper and a special coated film (for example, the glossy paper and the opaque white film which are used for the bright film list used for overhead location projection by high quality graphics and the pictorial output), and one fault has it. When the image field covering coat paper and the whole front face of a coated film was especially made from pigment system ink, a desiccation adhesive property and a humid adhesive property are poor, and having become the image which may become dirty easily was admitted. In recent years, the ink jet acceptor which combines high gloss and the high porosity rate for offering quick-drying capacity was developed. However, on a high gloss acceptor, length scratch dirt is more conspicuous. It is necessary to offer the pigment system ink constituent which can be used for the front face of an ink jet acceptance element printing the image which has the endurance and dirt-proof nature which were improved.

[0016] Generally ozone exists by the concentration of 10 – 50 PPB in the air in a sea level. An ozone level exceeds such level only under specific conditions. However, even in a low ozone level, when permeability is high, an ink jet color, colors, such as an ink jet pigment, and a pigment have very high susceptibility (for example, when printed by the porosity gloss acceptor), and fade sharply.

[0017] The ink jet acceptor designed for outdoor-type ways will fade sharply, if they are also exposed to ozone with high permeability, although there is an inclination to have good endurance when printed in pigment system ink.

[0018] A U.S. Pat. No. 5,716,436 specification and provisional publication of a patent In the 2000 No. -290553 official report, using a water-dispersion polymer in the ink jet ink printed by the regular paper is indicated. However, the image printed using these ink has low optical density, and its humid-proof abrasiveness is very inadequate, and it will not bear an outdoor-type way.

[0019] British ***** 2 351 292 No. is related with the ink jet ink constituent containing the water dissipation nature polymer which comes to contain a resultant. However, using these constituents on acceptors other than a regular paper is not indicated by this patent.

[Translation done.]

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] The purpose of this invention is offering the ink jet printing approach which uses the ink jet ink constituent containing a water-dispersion polymer, and the image printed by the front face of an ink jet acceptance element using this ink constituent has the ozone proof fastness and physical endurance (for example, scratch-proof nature and dirt-proof nature) which were improved.

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MEANS

[Means for Solving the Problem] The process which prepares the ink jet printer with which these purpose and other purposes answer A digital data signal, B) The process loaded with the ink acceptance element which comes to contain the base material which is supporting the ink absorbing layer of the porosity which has the continuous and same breadth which has a continuation void in the above-mentioned printer, C) The process which loads said printer with water, a wetting agent, a pigment, and the ink jet ink constituent that comes to contain the particle of a water-dispersion polymer, It is attained by this invention about the ink jet printing approach including the process which answers the D aforementioned digital data signal at a list, and is printed on said ink absorbing layer using said ink jet ink.

[0022] The image which has the ozone proof fastness and physical endurance (for example, scratch-proof nature and dirt-proof nature) which were improved by the ink jet printing approach of this invention which uses a porosity acceptor and the ink constituent containing the particle of a water-dispersion polymer is offered.

[0023]

[Embodiment of the Invention] The base material for the ink acceptance element used in this invention paper, resin coat paper, and plastics (for example, polyolefine type resin or polyester type resin (for example, polyethylene terephthalate) — Polycarbonate resin, polysulfone resin, methacrylic resin, cellophane, Acetate plastics, diacetyl cellulose, a cellulose triacetate, vinyl chloride resin, Polyethylenenaphthalate, polyester diacetate, various glass ingredients, etc. may include open pore structure (for example, thing made from polyolefine or polyester). The thickness of the base material used in this invention is 12 to 500 micrometer. It is 75 to 300 micrometer preferably. It can carry out.

[0024] the desirable voice of this invention — like — setting — the above — the ink absorbing layer of porosity with the continuous and same breadth contains the organic particle or the inorganic particle. A core / shell particle (for example, the [of Kapusniak for which it applied on June 30, 2000 / United States patent application] thing currently indicated in 09 / No. 609/969 specification), and a homogeneity particle (for example, thing currently indicated in the Europe ***** No. 0120331.3 specification) are contained in the example of the organic particle which may be used.

[0025] Acrylic resin, styrene resin, a cellulosic, polyvinyl resin, an ethylene-allyl compound copolymer, and a polycondensation polymer (for example, polyester) are contained in the example of the organic particle which may be used.

[0026] A silica, an alumina, a titanium dioxide, clay, a calcium carbonate, a barium sulfate, or a zinc oxide is contained in the example of the inorganic particle which may be used in this invention.

[0027] the desirable voice of this invention — like — setting — the above-mentioned porosity ink absorbing layer — 20% - 100% of particle, and 0% - 80% of giant-molecule binder — it comes to contain 80% - 95% of particle, and 20% - 5% of giant-molecule binder preferably the above-mentioned giant-molecule binder — a hydrophilic polymer (for example, polyvinyl alcohol —) A polyvinyl pyrrolidone, gelatin, cellulose ether, poly oxazoline, a polyvinyl acetamide and Pori hydrolyzed partially (vinyl acetate-co-vinyl alcohol) Polyacrylic acid, polyacrylamide, polyalkylene oxide, sulfonation or the polyester by which phosphorylation was carried out, and polystyrene, casein, a zein, albumin, a chitin, chitosan, a dextran, pectin, a collagen derivative, koro JIAN (collodian), an agar, an arrowroot, a gar,

carrageenan, tragacanth, xanthene, and Lamb Sun (rhamosan) etc. — you may be . Preferably, the above-mentioned hydrophilic polymers are polyvinyl alcohol, hydroxypropylcellulose, the hydroxypropyl methylcellulose, polyalkylene oxide, a polyvinyl pyrrolidone, polyvinyl acetate, these copolymers, or gelatin.

[0028] In order to give mechanical endurance to an ink jet record element, little addition of the cross linking agent which acts on the binder considered above may be carried out. Such an additive improves the bonding strength of a layer. For example, cross linking agents, such as a carbodiimide, a multi-functional value aziridine, an aldehyde, isocyanate, epoxide, a polyvalent metal cation, a vinyl sulfone, pyridinium, the pilus JIRIUMU (pyridylum) dication ether, a methoxy alkyl melamine, triazine, a dioxane derivative, chromium alum, and a sulfuric-acid zirconium, can be used. Preferably, a cross linking agent is an aldehyde, an acetal, or ketal (for example, 2, 3-dihydroxy -1,4-dioxane).

[0029] A porosity ink jet acceptance layer usually comes to contain the inorganic particle or the organic particle combined together with the binder as used in this specification. The amount of the particle in this type of coating is over critical particle volume concentration far in many cases, consequently the porosity rate of coating becomes high. In the ink jet printing approach, a liquid ink drop is absorbed quickly during coating by capillary action, and an image is in a set-to-touch condition immediately after coming out of a printer. Therefore, by porosity coating, quick "desiccation" of ink becomes possible and the image which has dirt-proof nature arises.

[0030] Moreover, the above-mentioned porosity ink absorbing layer can also contain open pore polyolefine, open pore polyester, or the open pore film. The open pore film can be made to form by known technique called phase inversion. the example of the porosity ink absorbing layer which comes to contain the open pore film — the Europe patent application 01202701.No. 7 — and — said — it is indicated in each specification of No. 01202711.6.

[0031] Independent or the organic pigment put together, and an inorganic pigment (for example, U.S. Pat. No. 5,026,427, ** No. 5,086,698, ** No. 5,141,556, ** No. 5,160,370 and ** what is indicated in each specification of No. 5,169,436) are contained in the pigment which may be used in this invention. It will depend for strict selection of a pigment on a specific application and engine-performance requirements (for example, color reproduction and image stability). To the suitable pigment for the use in this invention, for example, an azo pigment, a monoazo pigment, A disazo pigment, an azo pigment lake, a beta-naphthol pigment, the Naphthol AS pigment, A benzoimidazolone pigment and iso indoline (isoindoline) Pigment, A polycyclic type pigment, a phthalocyanine pigment, a quinacridone pigment, a perylene pigment, and a peri non pigment, A thioindigo pigment, an anthra pilus MIDON pigment, a flavanthrone pigment, Carbon black is contained in an anthanthrone (anthanthrone) pigment, a dioxazine pigment, a thoria reel carbonium pigment, a kino FUTARON pigment, a diketo pyrrolo pyrrole pigment, a titanium dioxide, ferrous oxide, and a list.

[0032] For the example of a type of the pigment which may be used A Color Index The pigment yellow 1, 2, 3, 5, 6, 10, 12, 13, 14, 16, 17, 62, 65, 73, 74, 75, 81, 83, 87, 90, 93, 94, 95, 97, 98, 99, 100, 101, 104, 106, 108, 109, 110, and 111, (C. I.) 113, 114, 116, 117, 120, 121, 123, 124, 126, 127, 128, 129, 130, 133, 136, 138, 139, 147, 148, 150, 151, 152, 153, 154, 155, 165, 166, 167, 168, 169, 170, 171, 172, 173, 174, 175, 176, 177, 179, 180, 181, 182, 183, 184, 185, 187, 188, 190, 191, 192, 193, 194;C.I. pigment Orange 1, 2, 5, 6, 13, 15, 16, and 17, 17: 1, 19, 22, 24, 31, 34, 36, 38, 40, 43, 44, 46, 48, 49, 51, 59, 60, 61, 62, 64, 65, 66, 67, 68, the 69;C.I. pigment red 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, and 14, 15, 16, 17, 18, 21, 22, 23, 31, 32, 38, 48:1, 48:2, 48:3, 48:4, 49:1, 49:2, 49:3, 50:1, 51, 52:1, 52:2, 53:1, 57:1, 60:1, 63:1, 66, 67, 68, 81, 95, 112, 114, 119, 122, 136, 144, 146, 147, 148, 149, 150, 151, 164, 166, 168, 169, 170, 171, 172, 175, 176, 177, 178, 179, 181, 184, 185, 187, 188, 190, 192, 194, 200, 202, 204, 206, 207, 210, 211, 212, 213, 214, 216, 220, 222, 237, 238, 239, 240, 242, 243, 245, 247, 248, 251, 252, 253, 254, 255, 256, 258, 261, 264; C. I. pigment violet 1, 2, and 3, 5: 1, 13, 19, 23, 25, 27, 29, 31, 32, 37, 39, 42, 44, the 50;C.I. pigment blues 1, 2, 9, 10, 14, 15:1, 15:2, 15:3, 15:4, 15:6, 15, 16, 18, and 19, 24: 1, 25, 56, 60, 61, 62, 63, 64, 66; C. I. pigment Green 1, 2, 4, 7, 8, 10, and 36, the 45;C.I. pigment blacks 1, 7, 20, 31, and 32, and C.I. pigment Brown 1, 5, 22, 23, 25, 38, 41, and 42 are contained.

[0033] The pigment used in the desirable mode of this invention is the C.I. pigment blue 15:3, the C.I. pigment red 122, the C.I. pigment yellow 155, the C.I. pigment yellow 74, and a screw. (free-wheel-plate ROSHIA nil alumino) They are tetra-phenyl disiloxane or the C.I. pigment black 7.

[0034] The aquosity dispersion medium for the ink constituent used in this invention is the mixture of

water or water, and at least one sort of water miscibility auxiliary solvents. It depends for selection of suitable mixture on a specific application (for example, the drying time of the ink jet ink in which desired surface tension and viscosity, the pigment chosen, and the pigment were added, the type of the paper in which ink is printed by the list). For the example of representation of the water miscibility auxiliary solvent which can be chosen (1) — alcohol (for example, methyl alcohol, ethyl alcohol, and n-propyl alcohol —) Isopropyl alcohol, n-butyl alcohol, sec butyl alcohol, T-butyl alcohol, isobutyl alcohol, furfuryl alcohol, and tetrahydrofurfuryl alcohol, (2) ketones, or keto alcohol (for example, an acetone —) A methyl ethyl ketone and diacetone alcohol, (3) ether (for example, a tetrahydrofuran and dioxane), (4) — ester (for example, ethyl acetate, ethyl lactate, and ethylene carbonate —) and propylene carbonate and (5) polyhydric alcohol (for example, ethylene glycol —) A diethylene glycol, triethylene glycol, tetraethylene glycol, Propylene glycol, a polyethylene glycol, glycerol, 2-methyl -2, 4-pentanediol, the low-grade alkyl mono-ether guided from 1, 2, 6-hexane triol and a thioglycol, and (6) alkylene glycol, and a low-grade alkyl diether (for example, the ethylene glycol monomethyl (or ethyl) ether —) The diethylene-glycol monomethyl (or ethyl) ether, the diethylene-glycol monobutyl (or ethyl) ether, The propylene glycol monomethyl (or ethyl) ether, polyethylene-glycol butyl ether, The triethylene glycol monomethyl (or ethyl) ether and the diethylene-glycol dimethyl (or ethyl) ether, (7) — a nitrogen content cyclic compound (for example, a pyrrolidone and an N-methyl -2-pyrrolidone —) And 1, 3-dimethyl (8) sulfur content compound (for example, dimethyl sulfoxide, 2, and 2'-thiodiethanol and a tetramethylen sulfone) is contained in -2-imidazolidinone and a list.

[0035] Generally it is desirable to make pigment system ink jet ink from the form of a thick mill grinding object, and this is diluted by behind suitable concentration to use it in an ink jet printing system. This technique enables it to prepare a lot of pigment system ink from equipment. When the above-mentioned mill grinding object is made in a solvent, it is diluted with water and other solvents in option, and it considers as suitable concentration. When the above-mentioned mill grinding object is made underwater, it is diluted with the further water or a water miscibility solvent, and it considers as desired concentration. Ink is adjusted to each viscosity desirable for an application, color, hue, saturated concentration, and printing field coating weight by dilution. About the preparation approach of a mill grinding object, they are U.S. Pat. No. 5,679,138 and **. No. 5,670,139 and **. It is indicated in each specification of No. 6,152,999. It is added by the ink jet ink constituent, and it is used for destroying a pigment in submicron magnitude in a grinding process, a colloid dispersing element is maintained at stability over a long period of time, and it is made for a dispersant not to have condensation in the desirable mode of this invention, either.

[0036] in the case of an organic pigment, ink can contain the pigment which attains to about 30 mass % — although kicked — general — almost all the ink jet printing application — setting — all ink constituents — about — 0.1 to 10 mass % — desirable — it is in the range of 0.1 – 5 mass % — I will come out. Generally, when an inorganic pigment is chosen, since an inorganic pigment has specific gravity higher than an organic pigment, ink tends to contain the pigment of higher mass %, and may serve as about 75% of high content from the equivalent ink which uses an organic pigment depending on the case.

[0037] the amount of the aqueosity dispersion medium used — the total mass of ink — receiving — about 70 to 99 mass % — it is in the range of about 90 to 98 mass % preferably. The mixture of water and polyhydric alcohol (for example, diethylene glycol) is useful as an aqueosity dispersion medium. In a desirable mode, ink contains the water miscibility solvent of 5 – 60 mass %. A percentage receives the total mass of an aqueosity dispersion medium.

[0038] the particle of the water-dispersion polymer used in this invention — general — 1 micrometer the following — desirable — 0.5 micrometers the following — more — desirable — 0.25 micrometers It has the mean particle diameter of the following.

[0039] Generally the water-dispersion polymer used in this invention may be a hydrophobic polymer of which [which may be stabilized in an aqueosity medium] presentation. Generally such a hydrophobic polymer is classified into either a condensation polymer or an addition polymer. Polyester, a polyamide, polyurethane, poly urea, a polyether, a polycarbonate, many acid anhydrides, and the polymer that comes to contain the combination of an above-mentioned type are contained in a condensation polymer. An addition polymer is the polymer formed of the polymerization of a

monomer vinyl type [, such as the ester guided from an allyl compound, vinyl ether, a vinyl heterocyclic compound, styrene an olefin and a halogenation olefin, ethylene system unsaturated carboxylic acid, and them, partial saturation nitril, vinyl alcohol, acrylamide and methacrylamide, a vinyl ketone, and a multi-functional value monomer,], or a copolymer formed from the various combination of these monomers.

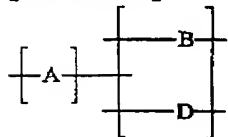
[0040] The styrene / acrylic polymer prepared according to the radical polymerization of the vinyl monomer in the inside of an aquosity emulsion are contained in the 1st class of desirable water-dispersion polymer. The suitable monomer for this styrene / acrylic polymer may be set to the technical field concerned, and is known as indicated for example, in the U.S. Pat. No. 5,594,047 specification. In the desirable mode of this invention, the monomer for this styrene / acrylic polymer is the ester of an acrylic acid, the ester of a methacrylic acid, styrene, or a styrene derivative.

[0041] For example, the monomer for above-mentioned styrene / acrylic polymer A methyl methacrylate, ethyl methacrylate, methacrylic-acid butyl, an ethyl acrylate, Butyl acrylate, acrylic-acid hexyl, acrylic-acid n-octyl, Methacrylic-acid lauryl, 2-ethylhexyl methacrylate, acrylic-acid nonyl, Methacrylic-acid benzyl, 2-hydroxypropyl methacrylate, acrylonitrile, A methacrylonitrile, vinyl acetate, propionic-acid vinyl, a vinylidene chloride, A vinyl chloride, styrene, t-butyl styrene, vinyltoluene, a butadiene, An isoprene, N,N-dimethylacrylamide, an acrylic acid, a methacrylic acid, Chloro methacrylic-acid, maleic-acid, allylamine, N, and N-diethyl allylamine, A vinyl sulfonamide, acrylic-acid sodium, sodium methacrylate, Acrylic-acid ammonium, methacrylic-acid ammonium, acrylamide propane-chlorination triethyl ammonium, Methacrylamide propane-chlorination triethyl ammonium, hydrochloric-acid vinylpyridine, Vinyl sodium phosphonate and 1-methylvinyl sodium phosphonate, Sodium vinylsulfonate, 1-methylvinyl sulfonic-acid sodium, 2-acrylamide -2-methyl It can be made to form from -1-propane sulfonic-acid sodium or styrene sulfonic-acid sodium.

[0042] An aquosity dispersibility polyester ionomer is contained in the 2nd class of water-dispersion polymer which may be used in this invention. In a desirable mode, these polyester ionomers have the following structures.

[0043]

[Formula 1]



[0044] It is the residue of one or more sorts of diol components which become together and come to contain A, and 100-mol % of a repeating unit among an upper type, and is expressed by the following structures.

[0045]

[Formula 2]

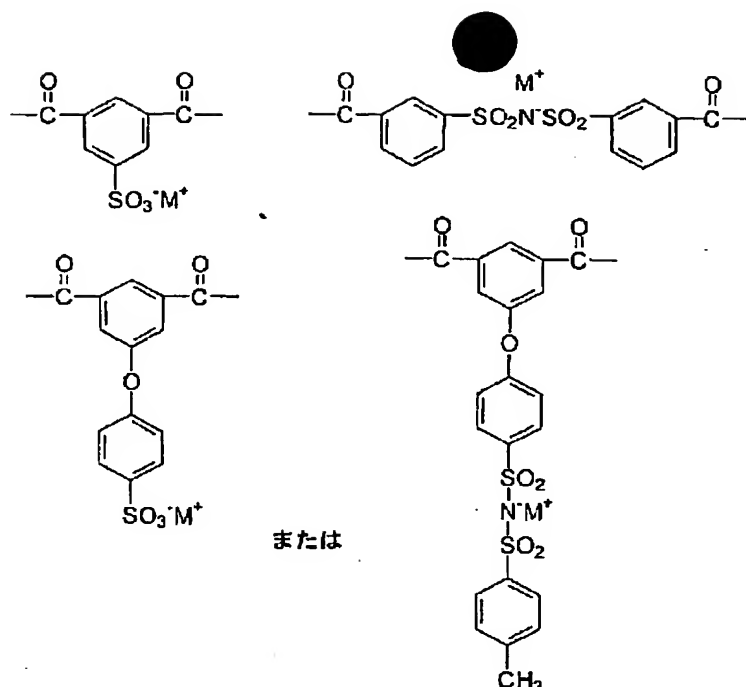


[0046] the inside of an upper type, and m and n — independent — the integer of 0-4 — expressing —
 - R1 The alkylene group which has 5 and 1-16 carbon atoms, the cyclo alkylene group which has 5-20 carbon atoms, The cyclo bis-alkylene group which has 8-20 carbon atoms, the bicyclo alkylene group which has 7-16 carbon atoms, or a tricyclo alkylene group, The bicyclo bis-alkylene group or tricyclo bis-alkylene group which has 9-18 carbon atoms, The arylene radical which has the arene bis-alkylene group which has 8-20 carbon atoms, or 6-12 carbon atoms, The poly dimethylsiloxane segment which has a carbitol end group is expressed, and it is R2. And R3 The aryl group which is not permuted [the permutation which has the alkyl group which is not permuted / the permutation which has H and 1-6 carbon atoms, or /, or 6-12 carbon atoms, or] is expressed independently respectively.

[0047] B is the residue of the diacid component which comes to contain 8-50-mol % of a repeating unit, and is expressed by one or more sorts of the following structures.

[0048]

[Formula 3]

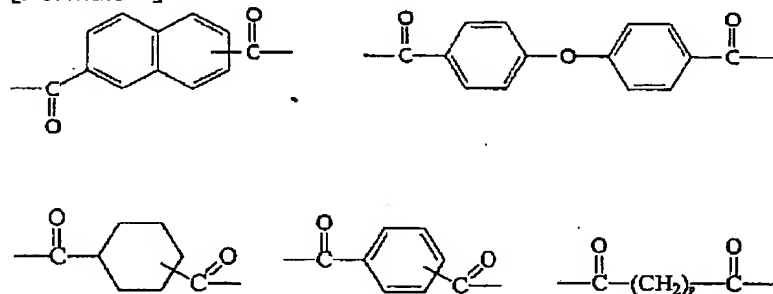


[0049] The inside of an upper type, and M⁺ Alkali metal (for example, Li, Na, and K), ammonium, a phosphonium (for example, ammonium, methylammonium, triethyl ammonium, tetra-alkylammonium, aryl trialkylammonium, etc.) radical (for example, triphenyl phosphonium, tetrabutyl phosphonium), complex aromatic series ammonium (for example, pyridinium, imidazolium, and N-methylammonium), a sulfonium radical, a GUANIDINIUM radical, a friend JINIUM radical, etc. are expressed.

[0050] D is the residue of the diacid component which comes to contain 50-92-mol % of a repeating unit, and is expressed by one or more sorts of the following structures.

[0051]

[Formula 4]



または

[0052] p expresses the integer of 2-12 among an upper type.

[0053] In the typical diol which A in the above-mentioned formula expresses Ethylene glycol, a diethylene glycol, triethylene glycol, Thiodiethanol, cyclohexane dimethanol, bisphenol A, Transformer -1, 4-cyclohexane diol, dodecane diol, Cis- - EKISO -2, 3-norbornane diol, 5-norbornene -2, 2-dimethanol, Hydroquinone screw (2-hydroxy ethyl ether) (Gelest Inc.) The poly dimethylsiloxane (MW=1000 (DMS-C15)) which has a carbitol end group is contained.

[0054] In this invention, Eastman AQ (trademark) polyester (Eastman Chemical Company) is contained in the example of useful water-dispersion polyester. Eastman polyester, AQ 29 (trademark), and AQ 38 (trademark) — and — AQ 55 (trademark) comes to contain isophthalic acid [of a different amount], sulfoisophtharate sodium, diethylene-glycol and 1, and 4-cyclohexane dimethanol. These thermoplastic amorphous ionicity polyester is prepared by an elevated temperature and low-pressure melting phase condensation polymerization, and this melting product is extruded by the small pellet. The minimum churning distributes easily in 70-degree C water, and this solid-state polymer produces the translucent hypoviscosity dispersing element which does not contain the

further surfactant or the further solvent at all. By changing the amount of an ionicity monomer (namely, sulfoisophtharate), particle size is controllable. Particle size is 0.02 to 0.1 micrometer. It migrates to the range.

[0055] Aqueosity dispersibility polyurethane is contained in the 3rd class of water-dispersion polymer which may be used in this invention. The example of useful polyurethane is indicated in the Europe patent application 01201186.No. 2 specification. These ingredients are "Polyurethane Handbook", Hanser Publishers, Munich Vienna, and 1985. It can prepare as indicated. The example of aqueosity dispersibility polyurethane is Witco Corp. It depends. A Witcobond (trademark) polyurethane dispersing element and BF Goodrich Company It depends. It is Sancure (trademark) polyurethane.

[0056] A polyurethane-acrylic polymer alloy is contained in the 4th class of water-dispersion polymer which may be used in this invention. The example of a useful polyurethane-acrylic polymer alloy dispersing element is indicated in the U.S. Pat. No. 5,173,526 specification. The example of this type of ingredient is based on CK Witco Corporation. It is Witcobond A-100 and this is an aliphatic series polyester alloy which uses urethane and polyacrylate as the base.

[0057] the water-dispersion polymer used in this invention — the inside of ink jet ink — general — 0.1 to 10 mass % — desirable — 0.5-5 mass % existence of is done.

[0058] Generally, in the printing field after these ink was printed, it was admitted by adding a water-dispersion polymer particle in ink that the gloss level of the front face of an acceptor could be raised.

[0059] Generally a jet rate, the separation length of a drop, the magnitude of a drop, and the stability of flow are influenced with the surface tension and viscosity of ink. Suitable pigment system ink jet ink to use it with an ink jet printing system should have the range of 20×10^{-5} – 60×10^{-5} N/cm (20 – 60 dyn/cm), and the surface tension which is in the range of 30×10^{-5} – 50×10^{-5} N/cm (30 – 50 dyn/cm) more preferably. Control of the surface tension in water color ink is attained by addition of a little surfactant. A simple trial-and-error experiment can determine the amount of the surfactant which should be used. U.S. Pat. No. 5,324,349, ** No. 4,156,616 and ** An anionic surface active agent and a cationic surface active agent can be chosen from other surface active agents known in the ink jet ink technical field by the thing list currently indicated in each specification of No. 5,279,654. Surfynol (trademark) of the product [surfactant / commercial] made from Air Products, and product made from DuPont Product made from Zonyl (trademark) and 3M Fluorad (trademark) is contained.

[0060] A wetting agent is used for the constituent used in the approach of this invention in order to help to prevent ink's hardening by drying or solidifying in the orifice of an ink jet print head. It sets to the constituent used in this invention for this purpose, and they are ethylene glycol, a diethylene glycol, triethylene glycol, propylene glycol, tetraethylene glycol, a polyethylene glycol, glycerol, and 2-methyl in a useful polyhydric-alcohol wetting agent. -2, 4-pentanediol, 1 and 2, 6-hexane triol, and a thioglycol are contained. A wetting agent can be used by the concentration of 10 – 50 mass %. In a desirable mode, the mixture of a diethylene glycol, or a glycerol and a diethylene glycol is used by the concentration of 10 – 20 mass %.

[0061] the above-mentioned ink has the physical property which suits an extensive radiation condition (namely, the drive frequency of the piezoelectric device in either the driver voltage in a thermal ink jet airline printer and pulse width, drop-on-demand type equipment or continuous system equipment and a list — the configuration of a nozzle, and magnitude).

[0062] Moreover, you may help to divide, when acceptor material is the paper to which sizing processing was performed highly, and to add a penetrating agent (zero to 10 mass %) to the ink constituent used in the approach of this invention, and for ink to permeate acceptor material. Concentration with a final penetrating agent desirable in the ink used in this invention is n-propanol of 1 – 6 mass %.

[0063] Moreover, a destruction-of-life agent (0.01 – 1.0 mass %) may be added to the ink constituent used in the approach of this invention, and growth of the microorganism which may be generated in ink by the passage of time and which is not desirable may be prevented. The last concentration of a destruction-of-life agent desirable in the ink used in this invention is Proxel(trademark) GXL of 0.05 – 0.5 mass % (Zeneca Colours Co.). A thickener, a conductive enhancement agent, a Kogation inhibitor, a drying agent, and a defoaming agent are contained in the further additive which may exist in option

in ink jet ink.

[0064] The ink jet ink manufactured using the water-dispersion polymer used in this invention is used in ink jet printing applied to ink acceptor material in the format by which the liquid ink drop was controlled by injecting a liquid ink drop from two or more nozzles (or orifice) which can be set to the print head of an ink jet printer.

[0065] How many differ is used for a commercial ink jet printer, and it is controlling adhesion of a liquid ink drop. Generally as such an approach, there are two kinds of types, a continuous-flow type and a drop-type on demand.

[0066] In a drop-on-demand type system, the drop of ink is directly injected from an orifice in one location of an ink absorbing layer with the piezoelectric device controlled according to a digital data signal, sound equipment, or the pressure generated by thermal **. A liquid ink drop is not generated until it is needed, and it is not injected from the orifice of a print head. The ink jet printing approach (and related printer) is marketed, and does not have the need of explaining to a detail.

[0067] The following examples explain the usefulness of this invention.

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EXAMPLE

[Example] The one or less-example pigment dispersing element was prepared.

[0069]

Magenta pigment dispersing element (MD-1) Mill grinding object 325 g Giant-molecule bead (average diameter = 50 micrometers)
(Tumbling media)

Quinacridone Magenta made from Sun Chemical Co. 30 g (pigment red 122)

Oleyl methyl taurine (OMT) potassium salt 9 g Deionized water 208 g Proxel GXL (trademark) 0.2g (destruction-of-life agent made from Zeneca)

[0070] the high energy medium mill manufactured by Morehouse-Cowles Hochmeyer in the above-mentioned component — using it — BYK-Gardner from — it ground in the obtained 2l. double-wall container. This mill was operated in the room temperature for about 8 hours. VWR Scientific Products from — obtained 4-8 micrometers By filtering the above-mentioned mill grinding object with a KIMAX (trademark) Buchner funnel, this dispersing element was separated from tumbling media.

[0071] a cyanogen pigment dispersing element (CD-1) — this dispersing element — instead of [of a Magenta pigment] — screw (free-wheel-plate ROSHIA nil alumino) Except for having used tetraphenyl disiloxane (Eastman Kodak Co.) and having used 18g OMT, it prepared like the above-mentioned Magenta pigment dispersing element.

[0072] a yellow pigment dispersing element (YD-1) — this dispersing element was prepared like the above-mentioned Magenta pigment dispersing element except for having used the pigment yellow 74 (Clariant Corporation) instead of the Magenta pigment, and having used 3.75g OMT.

[0073] the preparation polyester dispersing element 1 (PE-1) mechanical agitator of a water-dispersion polymer, an effective reflux condenser, and N2 It had the inlet. the 3 opening round bottom flask of 500mL — 5-sulfoisophtharate sodium of 28.96 g, isophthalic acid of 81.74 g, and the diethylene glycol of 45.37 g — and — It loaded with 46.51g cyclohexane dimethanol. It is this flask Slight N2 It placed into the salt bath of 220 degree C, agitating slowly under an air current. It is 0.51g when a reaction mixture dissolves. Fascat 4100 (trademark) catalyst is added and it is a polymerization. When it was made to go on for 8.0 hours, the water of the amount of theory was distilled off. It is this copolymer N2 It cooled rationally under the ambient atmosphere, next this polymer was taken out from the flask.

[0074] It had the mechanical agitator and the reflux condenser. The 3 opening round bottom flask of 250mL was loaded with the deionized water of 80mL, and it heated at 85 degrees C. Agitating quickly, the 20.3g above-mentioned polyester ionomer was added gradually, and this dispersing element was heated in 85 degrees C for 2 hours. Heating was set by the stop, this dispersing element was set to the room temperature, and it agitated all night. This mixture was filtered and 92.5g of dispersing elements containing the polymer of 18.7 mass % which bloomed cloudy slightly was obtained.

[0075] a polyester dispersing element 2 (PE-2) mechanical agitator, an effective reflux condenser, and N2 It had the inlet. the 3 opening round bottom flask of 500mL — 5-sulfoisophtharate sodium of 28.96 g, isophthalic acid of 81.74 g, and the diethylene glycol of 41.72 g — and — It loaded with 42.77g cyclohexane dimethanol. It is this flask Slight N2 It placed into the salt bath of 220 degree C, agitating slowly under an air current. It is 0.49g when a reaction mixture dissolves. Fascat 4100

(trademark) catalyst is added and it is a polymerization. When it was made to go on for 8.0 hours, the water of the amount of theory was distilled off. It is this copolymer N2 It cooled radiationally under the ambient atmosphere, next this polymer was taken out from the flask.

[0076] It had the mechanical agitator and the reflux condenser. The 3 opening round bottom flask of 250mL was loaded with the deionized water of 80mL, and it heated at 85 degrees C. Agitating quickly, the 20.1g above-mentioned polyester ionomer was added gradually, and this dispersing element was heated in 85 degrees C for 2 hours. Heating was set by the stop, this dispersing element was set to the room temperature, and it agitated for 20 hours. This mixture was filtered and 90.0g of dispersing elements containing the polymer of 19.1 mass % which bloomed cloudy slightly was obtained.

[0077] Polyester dispersing element 3 (PE-3) solid An AQ-55 polyester ionomer is purchased from Eastman Chemical, next it adds in water, heating and agitating, and is the concentration of 30% of solid content. AQ-55 dispersing element was obtained.

[0078] the start raw material which used the polyester dispersing element 4 (PE-4) polyester dispersing element 4 — 164.29g 1 and 4-cyclohexane dicarboxylic acid, sulfoisophtharate sodium of 46.30 g, and cyclohexane dimethanol of 90.24 g — and — 61.47g Except for having considered as 1 and 10-Deccan diol, it prepared according to the same procedure as the polyester dispersing element 2.

[0079] it had polyurethane dispersing element 1 (PU-1) agitator, the nitrogen inlet, and the condenser the flask of 500mL — 148.12g sulfoisophtharate sodium and 530.00g Tone (trademark)0200 (poly caprolactone polyol available from Union Carbide, molecular weight 530) — and — It loaded with the titanium (IV) isopropoxide of 200 ppm. It is this mixture, agitating. It heated at 250 degrees C. It is temperature when this mixture becomes transparence (about 2 hours). It raised to 270 degrees C and maintained for further 2 hours. When about 15.8g methanol condensates are collected, under [all / what / was completed mostly / an ester interchange]. It was used without having put this resultant (it being henceforth called SIP-diol) into the bottle, and refining it further.

[0080] a thermometer, an agitator, a water condenser, and the 2l. resin flask equipped with evacuation opening are loaded with 245.48g (0.19 mols) SIP-diol — in 100 degree C, it dehydrated under reduced pressure. This flask was placed into the bath by which temperature control was carried out. reduced pressure is solved and it sets at 40 degrees C — it added in the reaction flask, agitating 54.79g (0.24 mols) bisphenol A, 64.89g (0.72 mols) 1,4-butanediol, 2-butanone of 150g, and 40 drops of dibutyl tin JIRAU rates (catalyst). Temperature was raised to 82 degrees C, the homogeneous solution was obtained, and it cooled at 70 degrees C, then 226.74g (1.02 mols) isophorone diisocyanate and 10g 2-butanone were added.

[0081] Adjusted temperature, returned to 82 degrees C, maintained for 16 hours, the reaction was made to complete, and the final polyurethane which contains isolation isocyanate only less than 3% was obtained. The content of isolation isocyanate was supervised by infrared spectroscopy measurement of the absorption peak of the place of the wave number 2240. 2000g water was added under the high shear in this reaction flask, and the stable aquosity dispersing element was made to form. By heating under reduced pressure, 2-butanone was removed and the aquosity dispersing element of 40% of solid content was obtained.

[0082] Tone(trademark) 0260 (the poly caprolactone polyol available from Union Carbide, molecular weight 3000) of 123.0 g (0.041 mols) was put into polyurethane dispersing element 2 (PU-2) thermometer, the agitator, the water condenser, and the 2l. resin flask equipped with evacuation opening. This was dehydrated under reduced pressure in 100 degree C. Reduced pressure was solved, and the following were added, agitating in 40 degrees C. 22.70g (0.166 mols) dimethylol propionic acid, bisphenol A of 50.90 g (0.241 mols), 1,4-butanediol of 63.58 g (0.706 mols), 2-butanone of 180 g, and 20 drops of dibutyl tin JIRAU rates (catalyst). Raised temperature to 82 degrees C, maintained for 16 hours, the reaction was made to complete, and the intermediate field which contain isolation isocyanate only less than 3% were obtained.

[0083] The content of isolation isocyanate was supervised by infrared spectroscopy measurement of the absorption peak of the place of the wave number 2240. This reaction mixture was diluted with the 75g tetrahydrofuran, 19.7g of 45% of pottasium hydroxide solution neutralized, and 95% of theoretical ionization was attained to dimethylol propionic acid. Add 1300g distilled water under a high shear into this neutralized mixture, and made the stable aquosity dispersing element form, then it was made to

evaporate under reduced pressure, and 2-butanone was removed.

[0084] The polyurethane dispersing element 3 (PU-3) polyurethane dispersing element 3 prepared the used start raw material like the polyurethane dispersing element 2 except for having considered as 2 and 2-oxy-JIETA (dimethylol-propionic-acid [of 51.6g KM101733 (the polycarbonate polyol made from Stahl Co., m.w.860), and 10.20 g], and 10.0g) Norian, 1,4-butanediol of 24.33 g, and 111.20g isophorone diisocyanate.

[0085] Pori acrylic dispersing element 1 (PA-1) 400g deionized water — and — The 1l. 3 opening round bottom flask equipped with the mechanical agitator and the nitrogen inlet was loaded with Olin 10G (trademark) 0.6g surfactant. In the thermostatic bath, this solution was purged for 30 minutes with nitrogen, and was heated at 80 degrees C. a 172.8g methyl acrylate — and — 7.2g 2-acrylamide -2-methyl -1-propane sulfonic acid (sodium salt) was added, and it agitated for 3 minutes. 16.4g 10% sodium persulfate solution — and — The sodium-metabisulfite solution was added 10 5.5g%, and the polymerization was made to start. The polymerization was continued for 1 hour and it heated in 80 degrees C for further 1 hour. Temperature was lowered to 65-70 degrees C, and adding after mixing of t-butyl butyl hydroperoxide (10%) and the formaldehyde-sodium hydrogensulfite (10%) of 1mL was carried out respectively. This latex was cooled and filtered. This dispersing element contained the solid content of 30 mass %.

[0086] the Pori acrylic dispersing element 2 (PA-2) Pori acrylic dispersing element 2 — monomer mixture — methacrylamide of 14.17 g, the butyl acrylate of 106.2 g, and 2-acrylamide of 14.17 g -2-methyl -1-propane sulfonic acid (sodium salt) — and — The surfactant which should consist of 45.36g styrene and was used was prepared like the Pori acrylic dispersing element 1 except for having considered as sodium lauryl sulfate instead of Olin 10G. This dispersing element contained the solid content of 30 mass %.

[0087] The Pori acrylic dispersing element 3 (PA-3) Pori acrylic dispersing element 3 was prepared by mixing until 66g water and 9g triethanolamine, and the above-mentioned polymer dissolve completely Jonrez [J-4655 [25g] (styrene-acrylic polymer obtained from Westvaco Corporation).

[0088] 20-degree-C heating rate for /was used for the glass transition temperature (Tg) of a polymer property glass-transition-temperature desiccation polymer ingredient, and it measured it by the differential scanning calorimetry (DSC). Tg This specification is defined as point of inflection of glass transition.

[0089] About the particle of all particle-size measurement, it is rookhaven Instruments Corporation. It was manufactured. A property decision was made by 90plus Particle Sizer. Capacity average diameters are enumerated below.

[0090] The steric exclusion chromatography (SEC) in the inside of the tetrahydrofuran which uses three Polymer Laboratories plgl (trademark) small mixing (mini-mixed) B columns analyzed the average-molecular-weight above-mentioned sample. The molecular weight distribution of the group of this column, and 580-2,300,000 proofread using the narrow polystyrene criterion.

[0091] The various above-mentioned polymer properties are summarized to the following table I.

[0092]

[Table 1]

表 I

| ポリマー分散体 | 粒径 (nm) | 乾燥ポリマー の T _g (°C) | 重量平均 分子量 |
|--------------|------------|---------------------------------|-------------|
| ポリエステル分散体 1 | 308 | 23 | 3,400 |
| ポリエステル分散体 2 | 295 | 38 | 4,125 |
| ポリエステル分散体 3 | 19.9 | 55 | 18,000 |
| ポリエステル分散体 4 | 110.2 | 6 | 10,400 |
| ポリウレタン分散体 1 | 143.2 | 44 | 5,580 |
| ポリウレタン分散体 2 | 18.0 | 80 | 17,400 |
| ポリウレタン分散体 3 | 8.2 | 71 | 20,600 |
| ポリアクリル系分散体 1 | 100 | 25 | >1,000,000 |
| ポリアクリル系分散体 2 | 86 | 0 | >1,000,000 |

[0093] The ink formulation used in preparation this invention of ink was prepared by mixing agitating all components quietly in a room temperature. pH of final mixture is addition of triethanolamine. It adjusted to 8.5. everything but a pigment and a water-dispersion polymer — the glycerol of 10 mass %, and the triethylene glycol of 23 mass % — and — 2.5 mass % Ink was made to also contain Dowanol DPM (trademark).

[0094] The pigment and water-dispersion polymer which are used for the ink list used in this invention in three sorts of ink for a comparison are shown in the following table II.

[0095]

[Table 2]

表II

| インク | ポリマー分散体 | 顔料分散体 |
|------------|------------|------------|
| C-1 (対照標準) | 無し | CD-1 (2.5) |
| C-2 (対照標準) | 無し | MD-1 (2.9) |
| C-3 (対照標準) | 無し | YD-1 (2.9) |
| I-1 | PE-1 (2.5) | CD-1 (2.5) |
| I-2 | PE-2 (2.5) | CD-1 (2.5) |
| I-3 | PE-3 (2.5) | CD-1 (2.5) |
| I-4 | PA-1 (2.5) | CD-1 (2.5) |
| I-5 | PA-2 (2.5) | CD-1 (2.5) |
| I-6 | PU-3 (2.5) | CD-1 (2.5) |
| I-7 | PE-3 (2.5) | MD-1 (2.9) |
| I-8 | PE-4 (2.5) | MD-1 (2.9) |
| I-9 | PU-2 (2.0) | MD-1 (2.9) |
| I-10 | PA-3 (2.0) | MD-1 (2.9) |
| I-11 | PE-1 (2.5) | MD-1 (2.9) |
| I-12 | PU-1 (2.0) | MD-1 (2.9) |
| I-13 | PA-3 (2.0) | YD-1 (2.9) |

[0096] The ink jet record element acceptor 1 was made into the Xerox 4024DP regular paper (reference).

[0097] The acceptor 2 was made into the porosity gloss acceptor which comes to contain two layers in the polyethylene coat paper. a bottom member — fumed alumina, Cab-O-Sperse PG003 (trademark) (Cabot Corp.), polyvinyl alcohol, and GH-23 (Nippon Ghosei) and 2, and 3-dihydroxy the thing which comes to contain — 1,4-dioxane (Clariant Corp.) with the mass ratio of 87:9:4 — carrying out — thickness — 38 micrometers ** — it carried out. a top layer — Cab-O-Sperse PG003 (trademark) (Cabot Corp.), polyvinyl alcohol, GH-23 (Nippon Ghosei), and surfactant the thing which comes to contain Zonyl FSN (trademark) (DuPont Corp.) and the mordanting ingredient MM (to refer to the following explanation) with the mass ratio of 69:6:5:20 — carrying out — thickness — 2 micrometers ** — it carried out.

[0098] MM is chlorination N-vinylbenzyl of 87 mass %. — It is the bridge formation hydrogel polymer particle which is prepared from N, N, and N-trimethylammonium and the divinylbenzene of 13 mass % and whose mean particle diameter is 80nm.

[0099] An acceptor 3 and Epson Photoglossy Paper (trademark) It was referred to as SP91001 (Epson Corporation). This is a porous gloss acceptor.

[0100] An acceptor 4 is the sake of an outdoor-type way. It considered as EI Flame Retardant Banner (Eastman Kodak Company).

[0101] The acceptor 5 was made into EI Water Resistant Self-Adhesive Vinyl for an outdoor-type way (Eastman Kodak Company).

[0102] Acceptors 2-5 are ink acceptance elements which all come to contain the ink absorbing layer of the porosity which has the continuous and same breadth on a base material.

[0103] Ink was applied to the preparation above-mentioned acceptor 2 of the applied element, and it was made to dry these elements completely in 20-degree C indoor conditions before a trial by 16.3cm³/m² (16.3 cc/m²).

[0104] Humid-proof abrasiveness and the desiccation-proof abrasiveness above-mentioned ink were

applied on the above-mentioned ink jet record element. When a diameter wiped off superfluous water for the waterdrop which is about 2.54cm gently for [every] 2 minutes and after that on the front face of a sample on which ink was applied using a paper towel, the humid-proof abrasiveness trial was performed. Next, it is a diameter about the processed field like the above. On a 3.5cm field It ground against the paper towel which got dry under the pressure of 200g 8 times. The status A reflection density measured in the above-mentioned test area by the X-Rite (trademark) concentration meter was recorded, and it compared with the optical density before a trial. Humid-proof abrasiveness is defined as a percentage of the optical density (OD) held after a trial. 70% or more of humid-proof abrasiveness is desirable.

[0105] A desiccation-proof abrasiveness trial is a diameter about the above-mentioned sample. On a 3.5cm field Under the pressure of 200g, it carried out by grinding against the dry paper towel 8 times. The status A reflection density measured in the above-mentioned test area by the X-Rite (trademark) concentration meter was recorded, and it compared with the optical density before a trial. Desiccation-proof abrasiveness is defined as a percentage of the optical density (OD) held after a trial. 80% or more of humid-proof abrasiveness is desirable. About these results, it is the following table III. It enumerates.

[0106] Ozone resistance trial each sample was kept over 48 - 96 hours in the ozone chamber (amount of ozone 5 ppm, 50% of relative humidity, 21 degrees C). Before and after this ozone exposure test, it is X-Rite (trademark)414. The concentration meter was used and status A reflection density was measured. About the result of having calculated the retention (%) of status A concentration, it is the following table III. It reports. It is shown that it is so desirable that a numeric value is large, and the stability of the image to ozone exposure is more good.

[0107]

[Table 3]

表III

| インク 番号 | インク 中の ポリマー | インク 中の 顔料 | 湿潤耐久性 (濃度保持率) (%) | 乾燥耐久性 (濃度保持率) (%) | 48時間 耐オゾン堅牢度 (濃度保持率) (%) |
|-----------|-------------------|-----------------|-------------------------|-------------------------|-----------------------------------|
| G-1 | 無し | CD-1 | 57 | 52 | 29 |
| I-1 | PE-1 | CD-1 | 69 | 110 | 108 |
| I-2 | PE-2 | CD-1 | 76 | 89 | 101 |
| I-3 | PE-3 | CD-1 | 67 | 96 | 102 |
| I-4 | PA-1 | CD-1 | 94 | 106 | 104 |
| I-5 | PA-2 | CD-1 | 51 | 87 | 98 |
| I-6 | PU-3 | CD-1 | 103 | 104 | 102 |
| G-2 | 無し | MD-1 | 30 | 63 | 94 |
| I-7 | PE-3 | MD-1 | 71 | 99 | 98 |
| I-8 | PE-4 | MD-1 | 99 | 102 | 99 |
| I-9 | PU-2 | MD-1 | 90 | 100 | 99 |
| I-10 | PA-3 | MD-1 | 62 | 92 | 98 |
| G-3 | 無し | YD-1 | 73 | 68 | 100 |
| I-13 | PA-3 | YD-1 | 93 | 95 | 102 |

[0108] The above-mentioned result shows that abrasion resistance and ozone proof fastness were improved as compared with the element for a comparison in the ink containing the element and water-dispersion polymer which are using the porosity gloss acceptor 2 concerning this invention.

[0109] About a series of ink which has the component shown in two or less example, it is empty Hewlett-Packard HP 692C. It adds to an ink cartridge and is HP 692C. The printer was loaded and it printed on various acceptors. These samples were examined about humid endurance and ozone proof fastness. A result is shown in Table IV.

[0110]

[Table 4]

表IV

| 例 | ポリマー | 顔料 | 受容体 | 印刷試料の 光学濃度 | 漏洩耐久性 (濃度保持率) (%) | 96時間 耐オゾン堅牢度 (濃度保持率) (%) |
|------|------|------|-------------|---------------|-------------------------|-----------------------------------|
| C-2 | 無し | MD-1 | 1 (対照標準) | 0.94 | 紙が崩壊した | 92 |
| I-11 | PE-1 | MD-1 | 1 (対照標準) | 0.89 | 紙が崩壊した | 94 |
| I-7 | PE-3 | MD-1 | 1 (対照標準) | 0.92 | 紙が崩壊した | 98 |
| I-12 | PU-1 | MD-1 | 1 (対照標準) | 0.90 | 紙が崩壊した | 94 |
| C-2 | 無し | MD-1 | 2 | 2.41 | 18 | 91 |
| I-11 | PE-1 | MD-1 | 2 | 2.38 | 74 | 98 |
| I-7 | PE-3 | MD-1 | 2 | 2.50 | 82 | 100 |
| I-12 | PU-1 | MD-1 | 2 | 1.89 | 53 | 98 |
| C-2 | 無し | MD-1 | 3 | 2.24 | 65 | 88 |
| I-11 | PE-1 | MD-1 | 3 | 2.04 | 72 | 97 |
| I-7 | PE-3 | MD-1 | 3 | 2.28 | 94 | 99 |
| I-12 | PU-1 | MD-1 | 3 | 1.82 | 96 | 96 |
| C-2 | 無し | MD-1 | 4 | 1.30 | 100 | 84 |
| I-11 | PE-1 | MD-1 | 4 | 1.28 | 100 | 86 |
| I-7 | PE-3 | MD-1 | 4 | 1.31 | 100 | 92 |
| I-12 | PU-1 | MD-1 | 4 | 1.30 | 100 | 86 |
| C-2 | 無し | MD-1 | 5 | 1.25 | 100 | 83 |
| I-11 | PE-1 | MD-1 | 5 | 1.18 | 100 | 84 |
| I-7 | PE-3 | MD-1 | 5 | 1.19 | 100 | 92 |
| I-12 | PU-1 | MD-1 | 5 | 1.24 | 100 | 88 |

[0111] The ink in which the above-mentioned result was printed on the regular paper (acceptor 1) has low optical density, and when printed on the ink jet acceptor 2-5 to having produced the image in which endurance is inferior, it is shown that higher concentration and better endurance were accepted. Furthermore, when the ink containing a water-dispersion polymer used in this invention was used, amelioration of ozone proof fastness was accepted.

[0112] About a series of ink which has the component shown in three or less example, it is empty Hewlett-Packard HP 692C. It adds to an ink cartridge and is HP 692C. The printer was loaded and ink jet printing was carried out on the acceptor 2-5. These samples are examined about ozone proof fastness, and the result is shown in Table V.

[0113]

[Table 5]

表V

| インク | ポリマー | 顔料 | 受容体 | 96時間 耐オゾン堅牢度 (濃度保持率) (%) |
|-----|------|------|-----|-----------------------------------|
| C-1 | 無し | CD-1 | 2 | 73 |
| I-1 | PE-1 | CD-1 | 2 | 99 |
| I-2 | PE-2 | CD-1 | 2 | 98 |
| I-3 | PE-3 | CD-1 | 2 | 98 |
| C-1 | 無し | GD-1 | 3 | 61 |
| I-1 | PE-1 | GD-1 | 3 | 99 |
| I-2 | PE-2 | GD-1 | 3 | 98 |
| I-3 | PE-3 | GD-1 | 3 | 98 |
| C-1 | 無し | CD-1 | 4 | 41 |
| I-1 | PE-1 | CD-1 | 4 | 93 |
| I-2 | PE-2 | CD-1 | 4 | 91 |
| I-3 | PE-3 | CD-1 | 4 | 94 |
| C-1 | 無し | CD-1 | 5 | 49 |
| I-1 | PE-1 | CD-1 | 5 | 69 |
| I-2 | PE-2 | CD-1 | 5 | 67 |
| I-3 | PE-3 | CD-1 | 5 | 80 |

[0114] It is shown that the above-mentioned result has the ozone proof fastness containing a water-dispersion polymer by which the ink used in this invention was improved sharply.

[0115] Other desirable modes of this invention are indicated below in relation with a claim.

[0116] [1] The ink jet printer which answers A digital data signal The process loaded with the ink acceptance element which comes to contain the base material which is supporting the ink absorbing layer of the porosity which has the continuous and same breadth which has a continuation void in the process to prepare and the B aforementioned printer, C) The process which loads said printer with water, a wetting agent, a pigment, and the ink jet ink constituent that comes to contain the particle of a water-dispersion polymer, The ink jet printing approach including the process which answers the D aforementioned digital data signal at a list, and is printed on said ink absorbing layer using said ink jet ink.

[0117] [2] An approach given in [1] said water-dispersion polymer comes to contain polyester, polyurethane, or polyacrylate in.

[0118] [3] An approach given in [1] said porosity ink absorbing layer comes to contain 20% - 100% of particle, and 0% - 80% of giant-molecule binder in.

[0119] [4] An approach given in [1] said porosity ink absorbing layer comes to contain 50% - 95% of particle, and 50% - 5% of giant-molecule binder in.

[0120] [5] An approach given in [3] said particle comes to contain a silica, an alumina, a titanium dioxide, clay, a calcium carbonate, a barium sulfate, or a zinc oxide in.

[0121] [6] An approach given in [3] said whose giant-molecule binders are polyvinyl alcohol, hydroxypropylcellulose, the hydroxypropyl methylcellulose, polyalkylene oxide, a polyvinyl pyrrolidone, polyvinyl acetate, these copolymers, or gelatin.

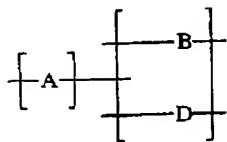
[0122] [7] An approach given in [1] in which said porosity ink absorbing layer contains the organic particle.

[0123] [8] An approach given in [1] the ink absorbing layer of porosity with the continuous and same breadth which has said continuation void comes to contain the macromolecule open pore film in.

[0124] [9] An approach given in [1] said water-dispersion polymer comes to contain a polyester ionomer in.

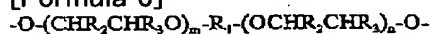
[0125] [10] Said polyester ionomers are the following general formulas. : [0126]

[Formula 5]



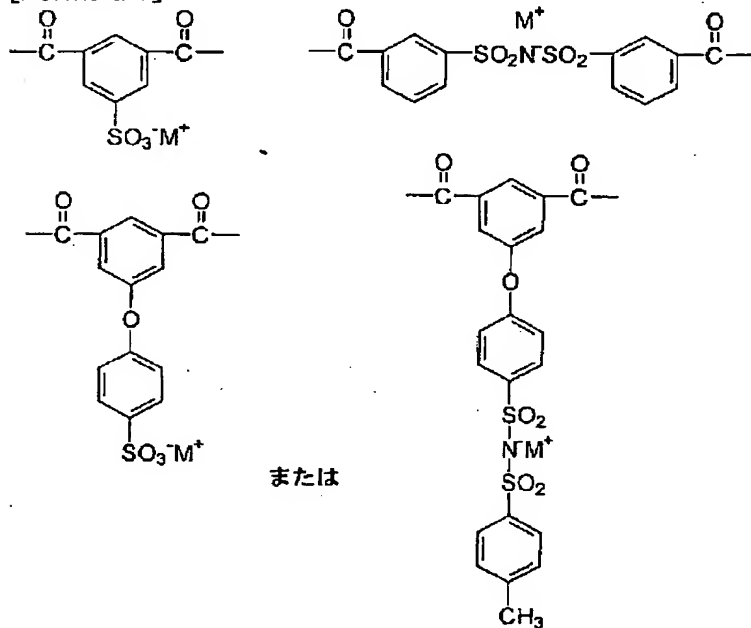
[0127] It is the residue of one or more sorts of diol components which ****, become together and come to contain A, and 100-mol % of a repeating unit among an upper type, and they are the following structures. : [0128]

[Formula 6]



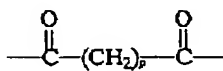
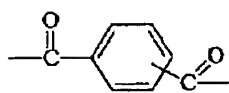
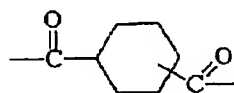
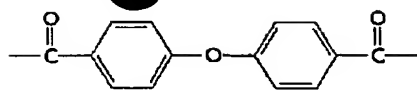
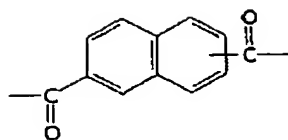
[0129] it expresses be alike — having — the inside of an upper type, and m and n — independent — the integer of 0-4 — expressing — R1 ** The alkylene group which has S and 1-16 carbon atoms, the cyclo alkylene group which has 5-20 carbon atoms, The cyclo bis-alkylene group which has 8-20 carbon atoms, the bicyclo alkylene group which has 7-16 carbon atoms, or a tricyclo alkylene group, The bicyclo bis-alkylene group or tricyclo bis-alkylene group which has 9-18 carbon atoms, The arylene radical which has the arene bis-alkylene group which has 8-20 carbon atoms, or 6-12 carbon atoms, the poly dimethylsiloxane segment which has a carbitol end group — expressing — R2 [and] And R3 Respectively, independently, it is the residue of the diacid component for which the aryl group which is not permuted [the permutation which has the alkyl group which is not permuted / the permutation which has H and 1-6 carbon atoms, or /, or 6-12 carbon atoms, or] is expressed, and B comes to contain 8-50-mol % of a repeating unit, and they are the following structures. : [0130]

[Formula 7]



[0131] It is expressed by one or more sorts of **, and they are the inside of an upper type, and M+. It is the residue of the diacid component for which alkali metal, ammonium, a phosphonium radical, complex aromatic series ammonium, a sulfonium radical, a GUANIJUMU radical, or a friend JINIUMU radical is expressed, and D comes to contain 50-92-mol % of a repeating unit, and they are the following structures. : [0132]

[Formula 8]



または

[0133] It is an approach given in [9] to which it is expressed by one or more sorts of **, and p expresses the integer of 2-12 among an upper type.

[Translation done.]

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